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Selected scientific information through early 1985 is presented and evaluated relative to the health and welfare effects associated with exposure to ozone and other photochemical oxidants.

Data on health and welfare effects are emphasized; additional information is provided for understanding the oxidant pollution problem, for evaluating the reliability of effects data, and for assessing effects data relative to concentration occurring in ambient air. Information is also presented on exposure-related topics: sources, measurement, and concentrations of oxidant precursors; formation and transport of ozone and other photochemical oxidants; properties, chemistry, and measurement of ozone and other photochemical oxidants; and the concentrations of ozone and other photochemical oxidants typically found in ambient air.

The specific areas addressed by chapters on health and welfare effects are the toxicological appraisal of effects of ozone and other oxidants; effects observed in controlled human exposures; effects observed in field and eipdemiological studies; and effects on vegetation, natural and agroecosystems, and nonbiological materials.

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ABSTRACT

Scientific information is presented and evaluated relative to the health and welfare effects associated with exposure to ozone and other photochemical oxidants. Although it is not intended as a complete and detailed literature review, the document covers pertinent literature through early 1985.

Data on health and welfare effects are emphasized, but additional information is provided for understanding the nature of the oxidant pollution problem and for evaluating the reliability of effects data as well as their relevance to potential exposures to ozone and other oxidants at concentrations occurring in ambient air. Information is presented on the following exposure-related topics: nature, source, measurement, and concentrations of precursors to ozone and other photochemical oxidants; the formation of ozone and other photochemical oxidants and their transport once formed; the properties, chemistry, and measurement of ozone and other photochemical oxidants; and the concentrations of ozone and other photochemical oxidants that are typically found in ambient air.

The specific areas addressed by chapters on health and welfare effects are the toxicological appraisal of effects of ozone and other oxidants; effects observed in controlled human exposures; effects observed in field and epidemiological studies; effects on vegetation seen in field and controlled exposures; effects on natural and agroecosystems; and effects on nonbiological materials observed in field and chamber studies.

AIR QUALITY CRITERIA FOR OZONE AND OTHER PHOTOCHEMICAL OXIDANTS

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6. EFFECTS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS ON VEGETATION

6.1 INTRODUCTION

An analysis of photochemical oxidants in the ambient air has revealed the presence of a number of phytotoxic compounds, including O_3, peroxyacyl nitrates, and NO_2. Ozone, the most prevalent photochemical oxidant, has received the most study and its effects are better understood than the effects of other photochemically derived oxidants. Ozone affects vegetation throughout the United States, impairing crops, native vegetation, and ecosystems more than any other air pollutant (Heck et al., 1980). The phytotoxicity of nitrogen oxides has been assessed in Air Quality Criteria for Oxides of Nitrogen (U.S. Environmental Protection Agency, 1982) and will not be discussed here. On a concentration basis, the peroxyacyl nitrates are more toxic than O_3, with PAN being about tenfold more phytotoxic than O_3 (Darley et al., 1963; Taylor and MacLean, 1970; Pell, 1976). Although more phytotoxic than O_3, the peroxyacyl nitrates generally occur at significantly lower ambient concentrations, however, and phytotoxic concentrations are therefore less widely distributed than those of O_3. Ambient concentrations of O_3 and PAN, as well as their concentration ratios, are discussed in detail in Chapter 5.

The effects of photochemical oxidants were first observed as foliar injury on vegetation growing in localized areas in Los Angeles County, California (Middleton et al., 1950). In these early reports, foliar injury was described as glazing, silvering, and bronzing of the lower leaf surface of leafy vegetables and as transverse bands of injury on monocotyledonous species. Subsequent studies showed that these symptoms of photochemical oxidant injury were caused by peroxyacetyl nitrate (Taylor et al., 1960). The characteristic O_3 stipple on grape leaves reported in the late 1950s was the first observation of O_3 injury to vegetation in the field (Richards et al., 1958). Subsequent studies with tobacco and other crops confirmed that O_3 was injuring vegetation at sites near urban centers (Heggestad and Middleton, 1959; Daines et al., 1960). It is now recognized that vegetation at rural sites may be injured by O_3 transported long distances from urban centers (Edinger et al., 1972; Heck et al., 1969; Heck and Heagle, 1970; Kelleher and Feder, 1978; Miller et al., 1972; Skelly et al., 1977; Skelly, 1980; see also Chapters 3 and 5).

The effects of O_3 and PAN on terrestrial vegetation may be envisioned as occurring at several levels, ranging from the molecular to the organismal, and then to the ecosystem level (Figure 6-1). The occurrence and magnitude of the vegetational effects depend on the concentration of the pollutant, the duration of the exposure, the length of time between exposures, and the various environmental and biological factors that influence the response. Some of the earliest observable physiological effects include altered membrane permeability, decreased carbon dioxide fixation (photosynthesis), and altered stomatal responses. These initial physiological changes are followed by inactivation or activation, or both, of specific enzymes, changes in metabolite pools, and alterations in the translocation of photosynthate. Biochemical changes within the plants are often expressed as visible foliar injury, premature senescence, increased leaf abscission, and reduced plant growth and yield. These changes at the individual plant level lead to altered reproduction, changes in competitive ability, or reduction of plant vigor. They subsequently are manifested by changes in plant communities and, ultimately, change in ecosystems. The sequence of topics in this chapter, which describes the effects of photochemical oxidants on plants, is based on the logical hierarchical ordering of plant responses depicted in Figure 6-1. The complexities of the entire subject are apparent in the sections on factors affecting plant response and on exposure-response relationships. Effects on terrestrial ecosystems are discussed in Chapter 7.

The linkages among altered biochemical processes, foliar injury, and reduced plant yield are not well understood. Likewise, no clear relationship exists between foliar injury and reduced plant yield for species in which the foliage is not part of the yield. The previous criteria document (U.S. Environmental Protection Agency, 1978) focused primarily on the effects of O_3 on physiological processes, foliar injury, and plant growth and attempted to summarize the literature by presenting limiting values (i.e., those concentrations below which foliar injury and, presumably, reduced growth and yield would not occur). In this document, the results of previous work on the effects of photochemical oxidants on physiological processes and on foliar injury and growth will be briefly summarized, with major emphasis placed on the effects of these oxidants on the intended use of the plant. Such effects are those that have impact on yield, quality, and aesthetic value.

The number of scientific reports on the effects of photochemical oxidants on vegetation has increased rapidly since the early 1960. In reviewing this extensive literature for the present revision, key references were selected for in-depth examination. For the most part, materials selected for review

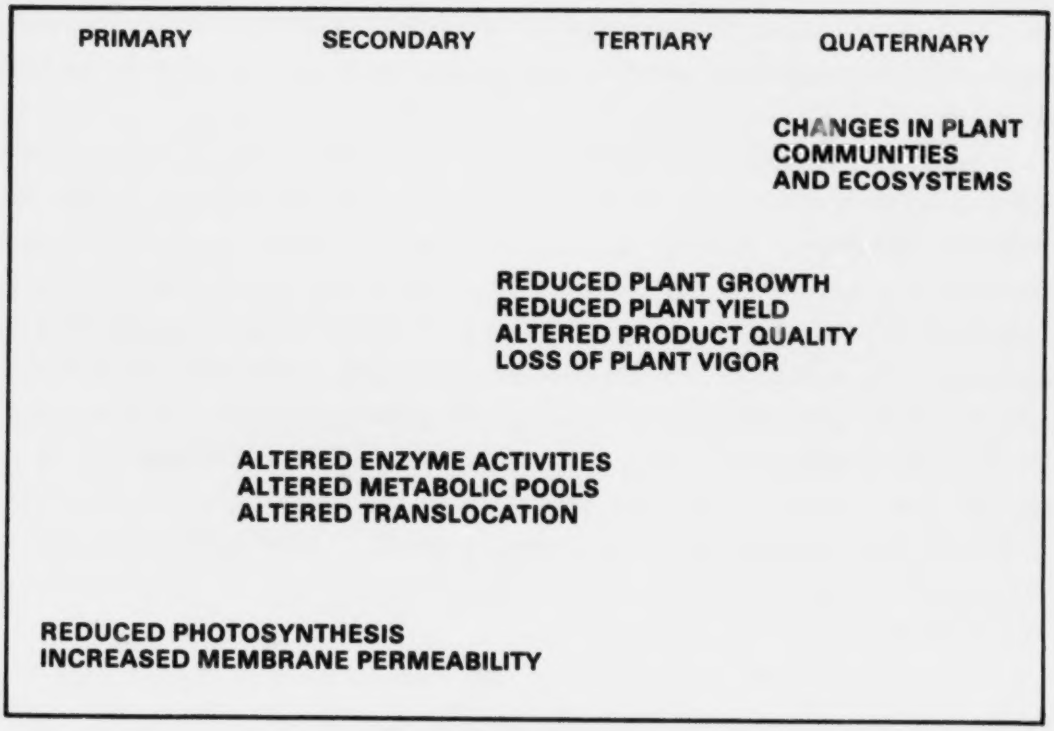

PRIMARY
SECONDARY
TERTIARY
QUATERNARY
CHANGES IN PLANT COMMUNITIES AND ECOSYSTEMS
REDUCED PLANT GROWTH
REDUCED PLANT YIELD
ALTERED PRODUCT QUALITY
LOSS OF PLANT VIGOR
ALTERED ENZYME ACTIVITIES
ALTERED METABOLIC POOLS
ALTERED TRANSLOCATION
REDUCED PHOTOSYNTHESIS
INCREASED MEMBRANE PERMEABILITY

Figure 6-1. Conceptual sequence of ozone-induced responses.

Source: U.S. Environmental Protection Agency (1978).

were publications that have appeared since the preparation of the 1978 criteria document. Earlier information considered fundamentally important is discussed and related to more recent studies. All data that relate exposure-response information to yield loss or crop loss were drawn directly from primary references, regardless of their citation in the 1978 criteria document. In this revision, crop loss refers to economic loss and yield loss refers to reductions in the quality, quantity, aesthetic value, or intended use of the crop. Generally, only published materials that have undergone scientific review have been cited.

Emphasis has been given to those studies in which the pollutant concentrations used were similar to those that occur in the ambient air of the United States. Therefore, studies in which the lowest concentrations of O_3 or PAN exceeded 1.0 ppm or 200 ppb, respectively, were not included unless the paper contained unique data, e.g., documentation of a mechanism involved in a specific response. In addition, in discussions on exposure-response data for the effects of O_3 and PAN on plant yield, the primary emphasis has been given to those studies reporting effects at concentrations below 0.25 ppm for O_3 and 40 ppb for PAN. These units have been used in the majority of the vegetational studies cited; conversion factors are: 1 ppm O_3 = 1960 $\mu g/m^3$ and 1 ppm PAN = 4947 $\mu g/m^3$. The scientific names of the plants cited in this chapter are listed in Appendix A.

Data used in the development of this chapter were derived from a diverse range of studies that were conducted to determine the effects of O_3 and PAN on various plant species and to characterize plant responses. The studies used a range of plant species and various experimental conditions and methodologies. Most important, it should be noted here that the studies cited were generally conducted to test specific biological hypotheses or to produce specific biological data rather than to develop air quality criteria.

In this chapter, the general methodologies used in studies of air pollution effects are discussed first, to provide a basis for understanding the methods, approaches, and experimental designs used in the studies presented later. Ozone and PAN are discussed separately, but the material presented for each will follow the same general outline, which includes (1) mode of action of the pollutant; (2) physical, biological, and chemical factors that alter plant response; and, the topic given primary emphasis, (3) the responses of plants exposed to various concentrations for various durations.

6.2 METHODOLOGIES USED IN VEGETATION EFFECTS RESEARCH

This section provides reference information for understanding better the studies discussed in the remainder of this chapter. The section contains an evaluation of exposure methods, a discussion of the strengths and limitations of various experimental designs and of the statistics used to represent pollutant exposures, and a discussion of the definitions of yield and crop loss. These discussions emphasize the methodologies used in studies cited in the chapter and do not reflect a general review of scientific literature. Changes in O_3 monitoring techniques, methods of calibration, quality assurance procedures, and their possible impacts on measured O_3 concentrations are discussed in Chapter 4.

6.2.1 Experimental Design and Statistical Analysis

The selection of an appropriate experimental design for specific objectives is a critical step in determining the success of a study and the application of the results. The number and kind of factors controlled, the patterns of randomization, and the number of replicates used in an experiment determine what treatment comparisons may be made, whether trends can be plotted and curves fitted, the precision of estimates, and the range of conditions over which inferences may be made. An experimental design focuses an experiment on its specific objectives, but in doing so, limits the application of the results. No experimental design has universal application.

Most experiments are of traditional designs amenable to the analysis of variance, such as randomized-block and split-plot designs. When used in conjunction with treatment mean separation techniques, these designs produce descriptive results that allow comparison of different treatments. There are many different treatment mean separation techniques available, such as Tukey's paired comparison procedure, Duncan's multiple range test, and Dunnett's test for comparing several treatments with a control. The tests all give slightly different results and have different powers. Some statisticians recommend careful inspection of the treatment averages in relation to a reference distribution in addition to or in place of formal multiple comparisons (Box et al., 1978). Few studies have attempted to partition interactions or to analyze slope and curvature trends. In factorial experiments with more than two factors, it has often been difficult to interpret the interactions fully.

Regression analyses are useful for many objectives, including the development of empirical models. Care must be taken, however, to ensure that there is no systematic deviation of the model from the observed data and to recognize that, in general, results cannot be extrapolated beyond the range of pollutant (e.g., ozone) concentrations used to construct the model. Both model validation (the testing of model fit to the experimental data) and applications validation (testing the application of the model to a new population) are appropriate precursors to model use.

In an experiment in which quantitative treatments are used and the treatments have been replicated, both analysis of variance and regression analysis may be used to analyze the data. The traditional approach is to use analysis of variance to estimate the error variance and to determine whether there are any differences among treatments; and then to break down the treatment effect into regression components to test whether there are any linear or quadratic trends as the treatment level changes (Cochran and Cox, 1957; Anderson and McLean, 1974). This is equivalent to doing analysis of variance followed by regression analysis. If a linear or quadratic equation does not fit the data well, or if there is a theorized functional relationship between treatment and response, nonlinear models may be fitted to the data at this point. Because each mathematical function can assume only a limited range of shapes, it is important to check for systematic lack of fit of the data. Confidence limits for regression curves can show the variability of the fitted curves. Confidence limits are frequently omitted from research papers, however, because their computation is complicated and it is difficult to show more than one curve in a figure if confidence limits are included. When confidence limits are not provided but results from similar experiments are available, the reader can obtain an idea of the variability of estimates by looking at the distribution of estimates from similar experiments. This variability encompasses sources of error beyond a single experiment.

In most of the papers cited in this document, confidence limits for exposure response curves were not provided. To compare the predictions of different exposure-response models, the O_3 concentrations that would cause 10 and 30 percent yield losses were calculated (see Section 6.4.3). These predicted concentrations also provide an indication of the relative sensitivity of the crop cultivar to O_3. For more sensitive plants, the 10 and 30 percent yield losses would be predicted to occur at lower concentrations. Therefore, a table of estimates from regression models of the O_3 concentration at which a 10 and 30 percent yield loss would occur for all the cultivars and species studied is included in the summary so that the reader can examine the range of estimates. On each graph the fitted curve is given, and generally the treatment means are also plotted. Where more than one model was fitted to the data, the reader may compare the results from the various models and observe whether there is a systematic lack of fit between the data and the curve. If a deviation is observed, the O_3 estimates may be biased.

The regression curves used in this document have either been calculated from the original observations or from treatment means. This distinction is noted in the figure legends whenever the method used is known. If the treatment means are used rather than the original observations in a linear regression and there are equal numbers of observations in each treatment, the results will be as follows: (1) the regression coefficients and estimated values will be the same as if individual points had been used; (2) the coefficient of variation (R^2) will be greater than or equal to the R^2 from individual points; and (3) the variance of the regression coefficients will be about the same as that computed from individual points if the variation of the means around the line is similar to the variation of individual points around the treatment means.

6.2.2 Exposure Characteristics

The occurrence of pollutants in the ambient air is influenced by many variables (see Chapters 3 and 5). Periods of significant air pollutant episodes occur when meteorological conditions, pollutant precursors, and other environmental conditions coincide. Ozone and PAN episodes usually occur during the plant-growth season (Chapter 5). The episodes may vary in duration from one to several days and occur at varying times of the day (Chapter 5). Research has not yet clearly defined which components of an exposure are most important in causing vegetation responses. The characterization and representation of plant exposures to air pollutants has been and continues to be a major problem. An appropriate summary statistic for one exposure duration usually cannot be easily transformed to describe a different exposure duration without access to the original aerometric data. In addition, statistics used to represent extremely short exposures cannot be readily aggregated to provide a representative summary statistic for plant responses resulting from an extended exposure (for example, a growing season).

6.2.2.1 Statistics Used to Characterize Seasonal Exposures. To define the problems associated with characterization and representation of plant exposures necessitates consideration of the temporal resolution required. When plant yield is considered, the ultimate impact of an air pollutant on yield depends on the integrated impact of the pollutant exposures during the growth of the plant. In this case, the temporal unit of interest becomes the plant growing season, which varies with the geographic location, plant species, and cultivar of interest. This period may be as short as 3 to 4 weeks for a crop such as radish or as long as years for perennial plants such as trees. Plants may be affected by exposures at several growth stages before harvest. Only a few studies have investigated the influence of plant growth stage on plant response to O_3. Studies with white beans in areas affected by photochemical oxidants indicated that crop maturity (plant growth stage) regulates the time of symptom expression and that crop vigor regulates the severity of the symptom (Haas, 1970). Petunia hybrids were less sensitive to O_3 after the flower bud differentiated (Hanson et al., 1975). Ozone reduced radish hypocotyl growth the most if the exposure occurred during the period of rapid hypocotyl growth (Tingey et al., 1973a). A single exposure to ozone produced a 37 percent reduction in hypocotyl growth in 14-day-old plants but less growth reduction in younger or in older plants.

If it is necessary to characterize the temporal distribution of pollutant concentrations within a growing season to characterize a plant response adequately, it is questionable whether the current exposure statistics used by researchers are adequate. Such regimens do not characterize the effects of pollutant episodes at specific and perhaps critical periods during plant growth. Statistics used to describe cumulative seasonal exposures, such as a seasonal mean, do not characterize the temporal distribution of the exposures within the season. Lognormal (Larsen et al., 1983) and two-parameter Weibull (Georgopoulos and Seinfeld, 1982; Rawlings and Cure, 1985) functions have been utilized to characterize seasonal exposures. These distribution functions are fitted to the seasonal mean O_3 concentrations without regard to their temporal order and therefore these functions, as well, do not characterize episodes within the season. Percentiles (number of hours at a given concentration range) (McLaughlin et al., 1982) can also be used to summarize the seasonal distribution of concentrations but these likewise provide no means of characterizing when within a season these episodes occur. The use of means (averages of concentrations over specific time periods) (Heck et al., 1982) and cumulative dose (Oshima et al., 1977a,b; Lefohn and Benedict, 1982) also ignores the episodic nature of seasonal exposures. Other exposure representations based on a seasonal averaging time suffer from similar inadequacies.

The difficulty of selecting an appropriate statistic to characterize plant exposure has been summarized by Heagle and Heck (1980). Ambient and experimental O_3 exposures have been presented as (1) seasonal, monthly, weekly, or daily means; (2) peak hourly means; (3) number of hours above a selected concentration; or (4) number of hours above selected concentration intervals. None of these statistics adequately characterizes the relationships among ambient O_3 concentration, exposure duration, and plant growth stages.

Until further research defines the influence on plant responses of temporal fluctuations in ozone concentrations, which is characteristic of exposures to ambient air, the selection of a summary statistic that characterizes ozone exposures will continue to be discretionary. Unfortunately, the existing summary statistics cannot be directly compared. Each is the result of calculations from the original aerometric monitoring data and cannot be transformed to another exposure statistic without the expensive and laborious task of returning to the original data. Therefore, comparisons among studies that use different summary statistics are difficult.

6.2.2.2 Statistics Used to Characterize Short Exposures. An experiment that focuses on foliar injury or any other relatively short-term response may only require short periods of exposure, which can be characterized by a simple exposure statistic. When such results are evaluated, a problem occurs only if the results of the short-term exposure experiment are extrapolated to evaluate their significance in relation to long-term exposures. Mean and dose (concentration multiplied by time) statistics from short-term exposures usually cannot be aggregated to be representative of the temporal dynamics of long-term exposures.

Although most short-term exposures are described by a concentration and duration of dose, scientists point out that the correct exposure representation is the amount of pollutant entering the plant, not the ambient air concentration to which it is exposed (Taylor et al., 1982a; Tingey and Taylor, 1982). Plants are affected only by the O_3 or PAN that diffuses into the leaves. It is difficult, however, to measure or quantify the relationship between the concentration of pollutant in the air and the internal pollutant flux because of the interactive effects of environmental and biological variables unique to a specific set of environmental conditions. An interactive model that requires variables describing the exposure, environmental condition, and species would be necessary to relate internal pollution flux to ambient air levels.

6.2.2.3 Evaluation of Exposure Statistics. The characterization and representation of plant exposures to O_3 has been and continues to be a major problem. As discussed above, in Sections 6.2.2.1 (Statistics Used to Characterize Seasonal Exposures) and 6.2.2.2 (Statistics Used to Characterize Short Exposures), several different exposure statistics have been used to characterize exposure. A mean concentration (with various averaging times) is the most common statistic used. Because the mean is computed by summing the concentrations and dividing by time, it mathematically treats all concentrations as being equally effective in causing a plant response. The use of a mean concentration (with varying averaging times) to characterize long-term expsoures minimizes the contributions of peak concentrations to the response by treating low-level, long-term exposures the same as high-concentration, short-term exposures. The use of a longer-term mean concentration ignores the importance of peak concentrations and is inconsistent with the literature.

A number of studies have shown that concentration is more important than exposure duration in causing a response. For example, studies with beans and tobacco (Heck et al., 1966) showed that a dose over a short time period induced more injury than the same dose distributed over a longer time period. Studies with tobacco showed that the O_3 concentration was substantially more important than exposure duration in determining the extent of foliar injury (Tonneijck, 1984). In this study, tobacco was exposed to a range of O_3 concentrations (0.02 to 0.15 ppm) for 8 hr/day for 1 to 7 days. In beans, foliar injury developed when the internal O_3 flux exceeded 115 μmoles/m^2 within 1 hr (Bennett, 1979). However, a single 3-hr exposure at about half the O_3 concentration (0.27 compared to 0.49 ppm) required approximately 64 percent greater internal O_3 flux to induce the same amount of foliar injury as in the 1-hr exposure (Bennett, 1979). Amiro et al. (1984) showed that higher concentrations were more important than low concentrations in causing injury. Their study also suggested the existence of a biochemical injury threshold (i.e., the O_3 uptake rates that plants can experience without inducing visible foliar injury). The greater importance of concentrations compared to exposure duration has been reported by other authors also (e.g., Heck and Tingey, 1971; Henderson and Reinert, 1979; Reinert and Nelson, 1979).

The total ozone dose (concentration multiplied by time) has been used to describe plant exposure; however, it suffers from the same problem as the mean. The total dose is simply the summation of the ppm-hr over the study period, which treats all concentrations as being equally effective. Several investigators have attempted to give greater importance to peak O_3 concentrations. Oshima et al. (1977a,b) and Lefohn and Benedict (1982), for example, have summed only the ppm-hr of exposure greater than some preselected value. Larsen et al. (1983) introduced the concept of "impact" to describe the effects of O_3 and SO_2 on soybeans. The "impact (I)" is calculated similarly to total dose, except that the concentration is raised to an exponent greater than one ($I = C^W \times T$); this method of calculation effectively gives greater weight to the higher concentrations. More recently, Larsen and Heck (1984) have suggested the term "effective mean" as an approach for describing the greater importance of higher concentrations. The "effective mean" is defined as the average hourly impact raised to an exponent and divided by the duration.

Several lines of evidence suggest that higher concentrations have a greater influence in determining the impact of O_3 on vegetation. Studies have shown that plants can tolerate some combinations of exposure duration and concentration without exhibiting foliar injury or effects on growth or yield, illustrating that not all concentrations are equally effective in causing a response. From the toxicological perspective, it is the peaks or concentrations above some level that are most likely to have an impact. Effects occur on vegetation when the amount of pollutant that the plant has absorbed exceeds the ability of the organism to repair or compensate for the impact.

Studies with soybean (Johnston and Heagle, 1982), tobacco (Heagle and Heck, 1974), and bean (Runeckles and Rosen, 1977) showed that plants exposed to a low level of O_3 for a few days became more sensitive to subsequent O_3 exposures. In studies with tobacco, Mukammal (1965) showed that a high ozone concentration on one day caused substantial injury but an equal or higher concentration on the second day caused only slight injury. Using stress ethylene as an indicator of O_3 effects, Stan and Schicker (1982) showed that a series of successive short exposures was more injurious to plants than a continuous exposure at the same O_3 concentration for the same total exposure period. Walmsley et al. (1980) continuously exposed radishes to O_3 for several weeks. They found that the plants acquired some O_3 tolerance. The acquired tolerance displayed two components: (1) the exposed plants developed new leaves faster than the controls and (2) there was a progressive decrease in sensitivity of the new leaves to O_3. The newer leaves also displayed a slower rate of senescence. The observations by Elkiey and Ormrod (1981) that the O_3 uptake decreased during a 3-day study period may provide an explanation for the results with radish.

Not only are concentration and time important but the dynamics of the O_3 exposure are also important; that is, whether the exposure is at a constant or variable concentration. Musselman et al. (1983) recently showed that fixed concentrations of O_3 cause the same kind of responses as variable concentrations at the equivalent dose. Fixed concentrations, however, had less effect on plant growth responses than variable concentrations at similar doses. Exposures of radishes to ambient O_3 in open-top exposure chambers showed that significant yield reductions occurred when the maximum O_3 concentration exceeded 0.06 ppm on at least 10 percent of the days when the crop was growing (Ashmore, 1984). Initial studies by Hogsett et al. (1985) have compared the response of alfalfa to daily peak and episodic O_3 exposure profiles which had the equivalent total O_3 dose over the growing season. Alfalfa yield was reduced to a greater extent in the episodic than the daily peak exposure. This study also illustrates the problem with the 7-hr seasonal mean concentration, which is that the peak concentrations are not properly considered. The plants that displayed the greater growth reduction (in the episodic exposure) were exposed to a significantly lower 7-hr seasonal mean concentration. Studies with SO_2 also showed that plants exposed to variable concentrations exhibited a greater plant response than those exposed to a constant concentration (McLaughlin et al., 1979; Male et al., 1983). These results suggest that the mechanisms causing the response are the same, but that exposures to fixed concentrations underestimate the magnitude of plant growth responses that can occur with episodic exposures.

Currently, there is no consensus as to the most appropriate summary statistic for representing plant exposure to photochemical oxidants. Consequently, many different statistics are used, making direct comparisons between studies extremely difficult. Further, there is some question as to the adequacy of statistics used to characterize long exposures (season), since they do not consider exposure dynamics within the period being represented. This question cannot presently be resolved because research to date has not clearly determined whether stages of plant growth are differentially sensitive to exposures relative to ultimate yield.

6.2.3 Exposure Systems

Research methods can be organized according to the means by which exposures or environmental variables are controlled or characterized. Air pollution research often requires exposure chambers or other apparatus for maintaining controlled pollutant exposures. Exposure systems may range from sophisticated, microprocessor-controlled cuvettes (Bingham and Coyne, 1977; Legge et al., 1979) to a series of tubes with calibrated orifices spatially distributed over a field to emit gaseous pollutants (Lee et al., 1978). Each type of systems was designed for specific objectives and operates most efficiently under the conditions for which it was intended. Each has advantages and limitations and must be evaluated in terms of the objectives it was designed to meet.

The exposure systems discussed in this section share many common characteristics. Each uses a monitoring system that measures pollutant concentration continuously during exposures or that incorporates a time-sharing system that sequentially measures concentrations in chambers or at field sites. The systems normally employ inert Teflon® tubing for sampling lines and continuous air flow to reduce time lags. Additionally, many systems use EPA-approved monitoring and detection systems (see Chapter 4 for EPA equivalent and Federal reference methods for ozone). Recently, quality assurance programs were included in several studies to ensure that high quality, standardized air monitoring data will be available and readily comparable. Under one such program, the air pollutants are generated artificially and dispensed to exposure chambers or field plots; under another, proportional activated-carbon filtration is used to provide different levels of ambient pollutants.

The systems described in this section represent significant advances in the methods used in air pollution research on vegetation. As systems that utilize the latest technological advances evolve, it is easy, because of the rapid pace of their evolution, to lose sight of their limitations. Even the most sophisticated and advanced systems are only as good as the researcher who uses them. They do not ensure that the research results will be of superior quality. They only provide the potential for understanding better the impact of air pollutants on vegetation.

The following discussion is limited to exposure systems used in air pollution research and is not meant to be a detailed description of the system components. These systems are described in greater detail in original publications and review articles (e.g., Heagle and Philbeck, 1979).

6.2.3.1 Laboratory Systems. Laboratory systems (Tingey et al., 1979; Winner and Mooney, 1980) typically employ artificial lighting and controlled environments. Most are designed to identify and measure effects ranging from the subcellular to the whole-plant level of biological organization. Although results from these systems are difficult to relate directly to field studies, they do contribute to an understanding of the mechanisms involved with air pollution effects. They provide useful information in explaining or interpreting responses. The stability of the well-controlled environmental conditions characteristic of most laboratory systems allows precise measurement of an array of plant responses. By altering only one variable and holding others constant, responses can be better defined and more easily understood. These systems are powerful tools for increasing the understanding of the effects of pollutants on the biological processes basic to plant growth.

The greatest drawback of laboratory systems relates to the general applicability of final results. The precise environmental conditions that make the systems valuable for defining responses also make the laboratory systems artificial. In comparison, ambient environmental conditions are complex and dynamic.

6.2.3.2 Greenhouse Exposure Systems. Greenhouse systems are generally used in studies to identify and quantify physiological, growth, and yield responses at the organ and whole-plant level of biological organization. Plants are usually grown in containers in greenhouses with charcoal-filtered air. Exposures are conducted under natural or artificial lighting, or both within chambers in the greenhouse. Plants may be physically moved in and out of exposure chambers and allowed to grow on greenhouse benches during interim periods. Normally, a single plant or small groups of plants constitute the experimental unit. While the environmental conditions of greenhouse exposure systems may more closely approximate field than laboratory conditions, the plant cultural conditions are more similar to those used in laboratory studies. Although related to field studies, greenhouse studies differ sufficiently to make direct extrapolations to field conditions difficult. It must be remembered, however, that greenhouse conditions are the typical cultural environment for many floricultural and ornamental plants. In this case, the use of greenhouse conditions is appropriate and no extrapolation is necessary.

Greenhouse exposure systems usually consist of a series of chambers built with a framework of various materials and covered with a transparent film. The air exchange systems normally use a negative pressure, single-directional air flow, and employ an activated-charcoal filtration device at both air entry and exhaust. Early systems were usually modifications of the system developed by Heck et al. (1968), but a variety of designs were utilized. These systems were all designed to meet common, desirable chamber characteristics (uniform pollutant concentrations with minimal environmental alteration) and succeeded to varying degrees. The design of the continuous stirred-tank reactor (CSTR) by Rogers et al. (1977) stimulated the development of exposure systems that incorporated its desirable mixing properties and the use of FEP Teflon® film as an inert polymer film.

6.2.3.3 Field Exposure Systems. The accurate assessment of pollutant-induced changes in agricultural productivity, and resulting economic impacts, requires that deviations from the ambient environment be minimized and that conditions characteristic of agricultural systems or natural ecosystems be simulated as closely as possible. Field exposure systems range from adaptations of the greenhouse and laboratory chamber designs to the use of chemical protectants. In most greenhouse and field studies, the investigators have attempted to ensure that soil moisture, plant nutrients, and other cultural conditions did not limit growth.

6.2.3.3.1 Field chamber systems. The open-top chamber system (Heagle et al., 1973; Mandl et al., 1973) is the most popular field-exposure system presently in use. Essentially upright cylinders with a clear polymer film as a covering around the sides, these chambers have the advantage of portability, moderate cost, and ease of maintenance. The size and shape of the chambers may be modified for use with different plant types and sizes. The system uses a high-volume flow of filtered air to reduce ambient pollutant influx through the open top. The chambers can be used as air-exclusion systems to test the difference between ambient air and charcoal-filtered air, or they can be used as exposure chambers, with pollutants added to the incoming air stream. The rate of pollutant addition is adjusted to control the pollutant concentration in the chambers. Pollutants are usually measured just above canopy height. Studies of the O_3 distribution within the chambers have shown it to be quite uniform. The vertical variation of O_3 concentration in the 2.44-m-high chambers was less than 6 percent between 0.3 and 1.2 m and less than 19 percent between 1.2 and 1.8 m. The horizontal variation over the 7.3 m^2 of the chamber was 12 percent and 14 percent at heights of 1.2 and 1.8 m, respectively (Heagle et al., 1979d). The portability of the system facilitates storage and maintenance during the winter or in periods of inactivity and allows standard agricultural practices to be carried out during field preparation, seeding, and early crop growth before chambers are set in place. Open-top chambers and well-ventilated, closed-top chambers reduce temperature deviations from the ambient, allow sufficient pollutant control for either single or mixed-gas exposures, and are relatively inexpensive. They can be selectively placed in established fields to avoid unacceptable soil types or to maximize soil uniformity in treatments.

Most of the limitations of open-top chambers relate to air-flow characteristics. Air flowing from the lower portion of the chamber out through the open top reduces the intrusion of outside air; this air-flow pattern is different, however, from that in the open field. Because plants in the chamber experience a different air-flow pattern than field-grown plants, concerns have been expressed that this might alter the influence of O_3 on plants. Recent measurements, however, of canopy resistance to O_3 uptake in open-top chambers and by micrometeorological methods in the field yield similar results of 73 and 84 sec m^{-1}, respectively (Unsworth et al., 1984a,b). This similarity led the authors to conclude that crop exposure to gaseous pollutants in open-top chambers is similar to that which would occur at the same concentrations in the field.

With open-top exposure chambers, some intrusion of ambient air and its pollutant burden through the chamber top is unavoidable; and this air can influence the pollutant concentrations within the chamber (Heagle et al., 1973; Unsworth et al., 1984a,b). The amount of intrusion increases with wind speed. Recent design innovations, however, have minimized this problem (Kats et al., 1976; Davis and Rogers, 1980). For example, the addition of a frustum (a truncated cone) to the top of the open-top chambers can reduce the intrusion of ambient air by approximately 50 percent and can also provide a more reproducible environment for a given wind speed (Unsworth et al., 1984a,b).

It should be recognized that open-field environmental conditions cannot be exactly duplicated by open-top exposure chambers (Heagle et al., 1979d; Olszyk et al., 1980) or any other pollutant exposure system presently available. In summarizing studies of open-top exposure chambers, Heagle et al. (1979d) reported:

> In our 7-yr experience, the open-top chambers caused plants to grow slightly taller but rarely had significant effects on yield. Plants often grew differently in different parts of the chambers but we did not find significant interactions between chamber position and the effects of O_3. The causes for chamber-induced growth effects may be related to slower mean air velocity, slightly higher temperature, or less light at some chamber locations than in the open.... There are no reports, however, that environmental changes of the magnitude caused by open-top chambers change plant sensitivity.
>
> (Heagle et al., 1979d)

The lack of a significant chamber influence on plant response is supported by the observation of Reich and Amundson (1984). They recently compared yield response functions for soybean exposed in a "tubular release system" with functions for soybean exposed in open-top exposure chambers, and concluded that the results from the two systems were comparable.

Other field-exposure systems use chambers of varying design, but have the common characteristic of being fully enclosed by film (Thompson and Taylor, 1966; Oshima, 1978). These designs rely on high air-exchange rates to minimize temperature alterations. Most of these designs are adaptations or alterations of greenhouse exposure systems. Chamber shapes range from a square design, as described by Heck et al. (1968), to the CSTR cylinder described by Rogers et al. (1977).

6.2.3.3.2 Field exposure systems without chambers. The desire to expose large field plots to increase sample size and to remove environmental alterations caused by enclosing plants in chambers led to the development of chamber-free field exposure systems. The advantage of these systems (Lee et al., 1978; deCormis et al., 1975; Reich et al., 1980; Laurence et al., 1982; Reich and Amundson, 1984) is that plants are exposed to pollutants under conditions similar to ambient conditions. This advantage is offset to some extent by the disadvantage of losing some control over pollutant concentration and the nature of the exposure. These systems are highly influenced by wind speed and direction, and are subject to ambient air levels. There have been only limited O_3 studies using these types of systems.

6.2.4 Methodologies Used in the National Crop Loss Assessment Network

The National Crop Loss Assessment Network (NCLAN) was initiated in 1980 by EPA to estimate the magnitude of national crop losses caused by air pollution. Initial emphasis was placed on O_3 (Heck et al., 1982). A research management committee has been responsible for the planning, management, and execution of the program. The primary objectives of the NCLAN program are:

1. To define the relationships between yields of major agricultural crops and O_3 exposure as required to provide data for economic assessments and the development of NAAQS;
2. To assess national economic consequences of the exposure of major agricultural crops to O_3; and
3. To advance the understanding of the cause and effect relationships that determine crop responses to pollutant exposure.

The NCLAN is a network of experimental field sites selected for (1) their different climatological conditions, (2) their distribution of different crop species, and (3) their proximity to established research groups with a history of research on air pollutant effects on vegetation. The test species are grown in the field under conditions approximating standard agronomic practices. Efforts are made to minimize perturbations of the plant environment by the exposure apparatus and to use realistic pollutant doses.

The pollutant concentrations around crop plants in the field are controlled and manipulated through the use of open-top chambers to simulate ambient exposures. Sufficient numbers of chambers permit replicated experimental designs; and also permit the development of empirical dose-response models. Models for test species and cultivars are developed from data for several sites and for several years.

Within the open-top chambers (see Section 6.2.3.3.1), plants are exposed to a range of ozone concentrations. Daily variations in the O_3 concentration are determined in part by changes in ambient O_3 concentrations at each site. The lowest O_3 concentration (control, charcoal-filtered air) is usually 20 to 50 percent of that in ambient air; the O_3 that is present enters the chamber mainly through the open top, because the inlet air to the chamber is charcoal-filtered. All other chambers receive ambient air supplemented (usually 7 hr/day) with enough O_3 to provide concentrations equal to those in the ambient air and three or four higher concentrations. Consequently, the O_3 exposures are coupled to ambient O_3 levels; days with the highest ambient O_3 will also be the same days when the highest concentrations will occur in a specific treatment in a chamber. As the ambient O_3 varies from day to day, the base to which additional O_3 is added also varies. This coupling of the O_3 exposures to the ambient environment means that high O_3 concentrations will occur in the chambers when the environmental and air chemistry conditions in the ambient air are conducive for producing elevated ambient O_3 levels.

In the initial NCLAN studies, O_3 was added to the chambers in three or four stepwise increments (0.02 to 0.03 ppm) above the concentration in the ambient air. In more recent studies, O_3 has been added at various proportions above the ambient concentration. The study by Temple et al. (1985b) illustrates both types of O_3 addition. Ozone concentrations within the chambers are measured at canopy height with time-shared monitors. Plant yields are also measured for non-chamber field plots of identical size exposed to ambient air to obtain an estimate of potential chamber effects. Chamber fans are operational from 5:00 a.m. to 9:00 p.m. daily, and O_3 is usually added from 9:00 a.m. through 4:00 p.m. (local standard time) daily throughout the growing season for the crop, except on rainy days.

A quality assurance program for the collection and measurement of air quality and biological data is followed in NCLAN studies. Independent audits of the pollutant monitors are conducted at each site.

The data are usually analyzed by regression analysis. The mean 7-hr daily concentration (9:00 a.m. to 4:00 p.m.), averaged over the growing season, is used for a seasonal exposure statistic. This is the time period when O_3 is added to the chambers.

Many strengths are associated with a coordinated national multisite program such as NCLAN. Perhaps the greatest strengths of NCLAN are the standardization of methods for air monitoring, biological assessment, experimental design, pollutant exposure regimes, summarization of exposures, and quality assurance. Additionally, the selection of agriculturally important crops for test species and the use of close approximations of standard cultural practices ensure applicability of experimental results. The development of empirical models interfaces well with the data requirements for a national economic assessment. Previously, very few biological models were available for economic assessments.

The NCLAN approach has limitations that must also be considered. The potential artificiality of the O_3 exposure treatments may complicate the application of results. Further, the use of the seasonal 7-hr daily mean concentration, a relatively new exposure summary statistic, makes comparisons with previously published studies difficult. It also does not accurately represent the temporal exposure dynamics of ambient air. The lack of validation of the model predictions is unsettling, but that is a common deficiency of all models to date and is not unique to NCLAN. These limitations may also occur with other field studies.

When viewed in perspective, NCLAN represents the state of the art for documenting yield losses resulting from ozone and for providing compatible data for use in economic assessments on a national scale.

6.2.5 Definitions of Yield Loss and Crop Loss

For the purposes of this chapter, yield loss is defined as reduction in quantity, quality, aesthetic value, or any impairment of the intended use of a plant. Thus, foliar injury on ornamental plants, detrimental responses in native species, and reductions in fruit or grain production by agricultural species are all considered yield loss. Crop loss, in contrast, is defined as an economic or monetary loss and is not synonymous with yield loss. Crop loss occurs at aggregative levels higher than the plant or plot. The transformation of yield loss to crop loss incorporates economic considerations such as those described in Section 6.4.2.2.3.

6.3 MODE OF ACTION OF OZONE ON PLANTS

Plant growth and yield are the culmination of many biochemical and physiological processes. Plants absorb carbon dioxide from the atmosphere through portals called stomata. Within the chloroplasts located in the mesophyll cells of the leaf (Figure 6-2), the carbon dioxide is converted into carbohydrates in the presence of light (photosynthesis). Plants absorb the necessary water and mineral nutrients for growth from the soil. Growth and yield depend not only on the rate of photosynthesis and the uptake of water and nutrients, but also on subsequent metabolic processes and the allocation of the photosynthetic products to the rest of the plant. The uptake of carbon dioxide and its subsequent metabolism and allocation within the plant are influenced by various environmental conditions. The impairment of any of these processes may affect plant growth and yield.

The responses of vascular plants to O_3 may be viewed as the culmination of a sequence of physical, biochemical, and physiological events. Ozone in the ambient air does not impair plant processes or performance, only the O_3 that diffuses into the plant. An effect will occur only if a sufficient

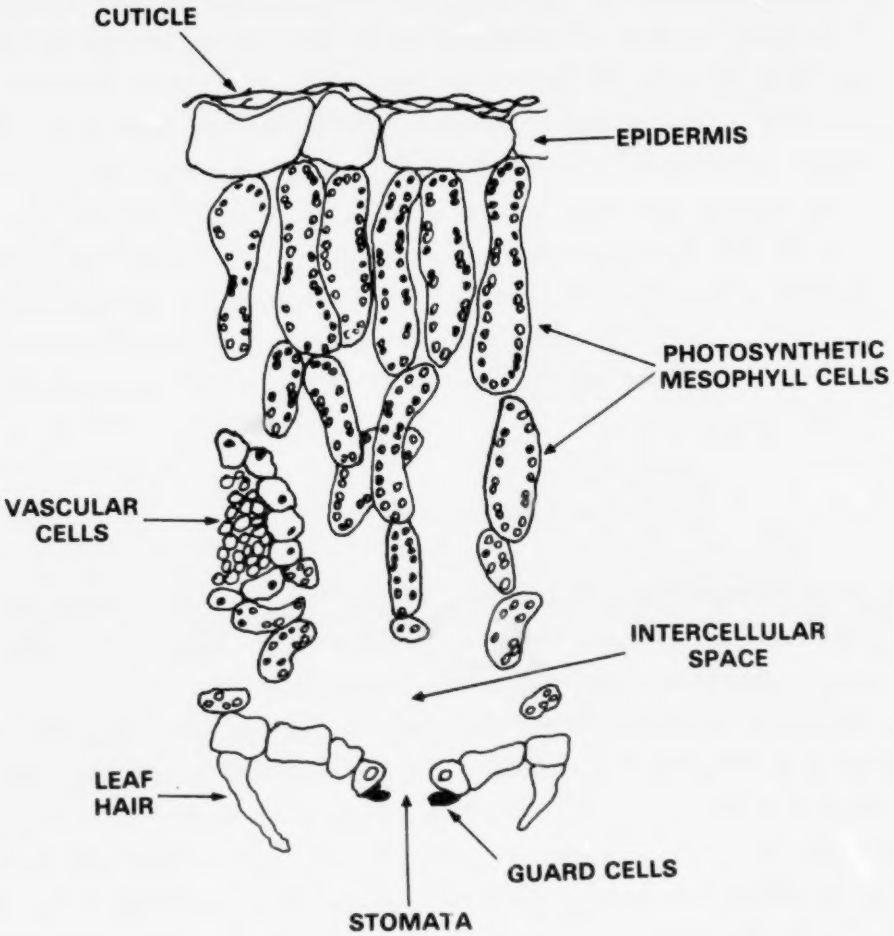

CUTICLE
EPIDERMIS
PHOTOSYNTHETIC MESOPHYLL CELLS
VASCULAR CELLS
INTERCELLULAR SPACE
LEAF HAIR
GUARD CELLS
STOMATA

Figure 6-2. Schematic cross section of a typical dicot leaf.

amount of O_3 reaches the sensitive cellular sites within the leaf. The O_3 diffuses from the ambient air into the leaf through the stomata, which can exert some control on O_3 uptake to the active sites within the leaf. Ozone injury will not occur if (1) the rate of O_3 uptake is sufficiently small so that the plant is able to detoxify or metabolize O_3 or its metabolites; or (2) the plant is able to repair or compensate for the O_3 impacts (Tingey and Taylor, 1982). The uptake and movement of O_3 to the sensitive cellular sites are subject to various physiological and biochemical controls.

Ozone enters the leaf through stomata; once within the leaf it quickly dissolves in the aqueous layer on the cells lining the air spaces. Ozone, or its decomposition products, then diffuses through the cell wall and membrane into the cell, where it may affect cellular or organellar processes. Ozone flux (J) into the leaf may be represented by the following equation (Tingey and Taylor, 1982):

$$J = \Delta C/(R_a + R_s + R_r). \tag{6-1}$$

Ozone flux is directly proportional to the change in O_3 concentration (ΔC) between the ambient air and the leaf interior (gas-to-liquid transfer) and is inversely proportional to resistance to the mass transfer of gas. Resistance to O_3 movement can be divided into components, including boundary layer (R_a), stomatal and intercellular space (R_s), and liquid-phase (R_r) resistances.

At any point along this pathway, O_3 or its decomposition products may react with cellular components. Altered cell structure and function may result in changes in membrane permeability, carbon dioxide fixation, and many secondary metabolic processes (Tingey and Taylor, 1982). The magnitude of O_3-induced effects will depend upon the physical environment of the plant, including macro- and microclimatic factors; the chemical environment of the plant, including other gaseous air pollutants and a variety of chemicals; and biological factors, including genetic potential and developmental age of the plant and interaction with plant pests. Cellular injury may subsequently manifest itself in a number of ways, including visible foliar injury, premature senescence, reduced yield or growth or both, reduced plant vigor, and sometimes death. Depending upon the intended use of a plant species (i.e., for food, forage, fiber, shelter, or amenity), any of the effects discussed above could impact society adversely.

In the following sections, selected references will be cited to describe how O_3 induces some of its effects. Some of the physiological studies have been conducted with O_3 exposures that would rarely, if ever, be encountered in ambient air. This literature can, however, serve as a tool for identifying the potential sequence of the physiological and biochemical responses of plant species, and for identifying potential metabolic sites of action.

6.3.1 Biochemical and Physiological Responses to Ozone

Phytotoxic effects of air pollution on plant tissue will occur only when sufficient concentrations of a gas diffuse into the leaf interior and pass into the liquid phase of the cells. Once a gas is deposited on a wet cell surface, it may move by diffusion or bulk flow to sites of action, such as the interior of the cell membrane, the cytoplasm, or cellular organelles (Heath, 1980; Tingey and Taylor, 1982).

6.3.1.1 Gas-Phase Movement into the Leaf. Ozone, as well as other gases, diffuses from the atmosphere into the leaf through stomata. The stomata control the rate of O_3 uptake into the leaf and are influenced by various plant and environmental stimuli. A variety of factors, including O_3, have been shown to induce stomatal closure. The previous criteria document (U.S. Environmental Protection Agency, 1978) cited a number of studies that directly correlated O_3 concentration and stomatal closure. Engle and Gabelman (1966) reported that in the presence of O_3 (0.3 ppm for 0.5 hour) stomata closed more quickly in tolerant than in sensitive onion cultivars. Rich and Turner (1972) found that when tobacco plants were exposed to 0.20 to 0.25 ppm O_3 for 2 hours, leaf conductance (a measure of stomatal closure) decreased 32 percent in a resistant cultivar and only 9 percent in a sensitive cultivar (no statistics provided), suggesting possible differences in O_3 uptake between cultivars. In contrast, when four cultivars of peas were exposed to an O_3 concentration of 0.15 ppm for 6 hours per day and stomatal conductance was measured, the two more sensitive cultivars had greater decreases in leaf conductance (85 percent and 86 percent) than did the two more tolerant cultivars (62 percent and 69 percent) (Dijak and Ormrod, 1982). Clearly, decreased conductance could not explain differential cultivar tolerance in this case. More recently, Krause and Weidensaul (1978b) observed that geranium guard cells, which control stomatal opening, ruptured after a 10-day exposure to O_3 at concentrations of 0.15 ppm for 6 hours per day. When they reviewed the O_3 uptake literature, Tingey and Taylor (1982) found examples of species for which the O_3 response was apparently limited by leaf conductance (i.e., O_3 uptake) and species for which O_3 response (injury) was not controlled by O_3 uptake but rather by metabolic processes within the mesophyll cells.

Ozone flux into the leaf may also be regulated by stomatal density. Butler and Tibbitts (1979a,b) correlated stomatal density directly with O_3-induced visible injury in bean plants, but Gesalman and Davis (1978) found no such relationship for azalea cultivars. There was no apparent relationship between stomatal frequency or guard-cell length and differential O_3 sensitivity in two corn cultivars (Harris and Heath, 1981). They found that the leaf water potential was poised near the point at which only a slight water loss in the tolerant cultivar would induce stomatal closure. Hence, they suggested a rapid stomatal closure in response to an O_3-induced water loss. In the 1978 criteria document (U.S. Environmental Protection Agency, 1978), equally disparate results were offered for several plant species. Dean (1972) reported that tobacco cultivars that exhibited tolerance to oxidant-induced weather fleck in the field had lower stomatal density than that in sensitive cultivars. Evans and Ting (1974) found that the maximum O_3 sensitivity of primary leaves of bean could not be accounted for by stomatal density.

In summary, different plant responses to O_3 are in part the result of the diffusion of O_3 into the leaf interior. A knowledge of the O_3 uptake rate or amount, however, is not sufficient for predicting subsequent responses for all species. In some species, injury is apparently not directly related to O_3 uptake; in others, there is a relationship between the quantity of O_3 entering the plant and the degree of subsequent injury. The physical and chemical environment and biological potential of the plant influence stomatal behavior and O_3 uptake, as will be documented in later sections. Once O_3 enters the plant, there are potential reactions with many cellular constituents.

6.3.1.2 Transition between Gas-Phase and Liquid-Phase Movement into the Cell.

Once ozone enters the intercellular spaces, it passes into the liquid phase at the gas-liquid interface of the cell wall surface. The diffusive process is dependent on physical, chemical, and biological factors that govern this diffusive step (Tingey and Taylor, 1982). The solubility of O_3 is critical to further reaction and depends on microclimatic factors, including temperature.

The rate at which gas diffusion occurs may also depend upon the internal cell surface area exposed (Evans and Ting, 1974; Pell and Weissberger, 1976; Uhring, 1978). Taylor et al. (1982b) reported that in soybean foliage pollutant flux was not regulated solely by the number of cellular sites of O_3

deposition. When plants were exposed to O_3 concentrations ranging between 0.25 and 0.58 ppm for 1 to 4 hours, uptake rates were higher and the ratio of internal/external leaf area was lower for "Hood," a relatively tolerant soybean cultivar, than for "Dare," which was more sensitive. Athanassious (1980) did not identify surface-volume ratio as a determinant of relative response of radish mesophyll cells to O_3, but suggested that differential suberization of cell walls may explain relative sensitivity of parenchymal tissue. This idea was offered previously by Glater et al. (1962).

6.3.1.3 Chemical and Biochemical Responses. When O_3 passes into the liquid phase, it undergoes transformations that yield a variety of free radicals, including superoxide and hydroxyl radicals (Pryor et al., 1981; Hoigne and Bader, 1975; Tingey and Taylor, 1982). Whether these chemical species result from decomposition of O_3 or reactions between O_3 and biochemicals in the extracellular fluid has not been determined. Ozone or its decomposition products, or both, will then react with cellular components, resulting in structural or functional effects, or both.

The potential for O_3, directly or indirectly, to oxidize biochemicals *in vitro* has been demonstrated. Ozone can oxidize a number of biological molecules, including reduced nicotinamide adenine dinucleotide (NADH), DNA, RNA, purine, pyrimidines, indole acetic acid, some amino acids (including tryptophan and methionine), many proteins (including enzymes such as glyceraldehyde-3-phosphate dehydrogenase, catalase, peroxidase, papain, ribonuclease, and urease), and a variety of lipids (Christensen and Geise, 1954; Todd, 1958; Ordin and Propst, 1962; Heath, 1975; Mudd, 1982). In these and similar studies, the concentrations of O_3 bubbled into the biochemical solutions were all very high. It is difficult to compare the exposure to ozone in solution to the ambient air exposure that plants experience. Coulson and Heath (1974) have suggested, however, that solution and atmospheric exposures are not highly dissimilar. They showed that most of the O_3 bubbled into solutions exited unreacted and that the O_3 dose required to injure cells in solution was of a magnitude similar to that required to injure intact plants exposed to atmospheric O_3. Todd (1958) predicted sensitivity within the plant by relating concentrations of protein used *in vitro* to levels in the plant, and then extrapolating to lower concentrations of O_3. Similar comparisons could be made for other biochemicals studied *in vitro*. Because biochemicals are compartmentalized within the plant, such calculations of potential sensitivity may deviate from actual responses observed. Data acquired from *in vitro* studies are best utilized to demonstrate that many cellular constituents are susceptible to oxidation by O_3. Different approaches will have to be used to determine which, in fact, are important *in vivo*.

The potential for biochemicals to be affected within the plant has been explored by a number of researchers. Increases and decreases have been observed in the status of proteins, sulfhydryl residues, fatty acids, and sterols (Pell, 1979; Trevathan et al., 1979; Swanson et al., 1973). Results vary among laboratories. For example, Trevathan et al. (1979) observed a decrease in fatty acids 3 days after tobacco plants were exposed to 0.24 ppm O_3 for 6 hours, whereas Swanson et al. (1973) detected no change in fatty acid content in the same species 2 hours after plants received 0.30 ppm O_3 for 2 hours. It is likely that Trevathan et al. (1979) were observing a late plant response associated with injury and cell death while Swanson et al. (1973) were finding evidence that lipids were not particularly sensitive to O_3. Similarly, Fong and Heath (1981) were unable to detect any changes in either phospholipid content or fatty acid composition of total polar lipids in bean leaves that sustained mild visible injury after exposure to an O_3 concentration of 0.30 ppm for 1 hour. Changes in mono- and digalactolipids were observed after severe injury was induced by a concentration of 0.50 ppm for 1 hour.

The examples above serve to underscore the importance of recognizing the limitations of studies in which biochemical effects are determined for whole leaf tissue rather than for organelles; or in which effects are determined in terms of cell function. Such data neither describe the dynamics of injury development nor identify the cellular site at which biochemical changes are occurring. This kind of biochemical information is useful, however, in characterizing the nature of a response to O_3 as it relates to altered metabolism, in general, and to visible foliar injury.

6.3.1.4 Physiological Responses. Physiological measurements have been more useful than biochemical quantifications in characterizing cell responses to oxidants. Many consider membranes to be the primary site of action of O_3 (Heath, 1980; Tingey and Taylor, 1982). The alteration in plasma membrane function is an early event in the sequence of O_3-induced effects that eventually leads to leaf injury and subsequent yield loss. Changes in the semipermeability of the membrane are evidenced by changes in fluxes of carbohydrates, amino acids, inorganic ions, and water (Heath, 1975, 1980; Tingey and Taylor, 1982). Whether the plasma membrane or some organelle membrane is the primary site of O_3 action is open to speculation (Tingey and Taylor, 1982). Mudd

(1982) suggested that O_3 or its decomposition products may penetrate the plasma membrane and injure organelles. A number of membrane-dependent functions of organelles can be altered by O_3. MacDowall (1965) reported that oxidative phosphorylation was inhibited when tobacco plants were exposed to O_3 at concentrations from 0.6 to 0.7 ppm for 1 hour. Photophosphorylation was inhibited in isolated spinach chloroplasts when O_3 (400 ppm for 15 minutes) was passed through the chloroplast suspension (Coulson and Heath, 1974). Using the Bensen coefficient for O_3 and the partial pressure of the gas above the aqueous solution, Coulson and Heath (1974) calculated the latter dose to be equivalent to a concentration of 0.20 ppm in ambient air surrounding a terrestrial plant.

Ozone can also affect biochemical functions not associated with membranes. The activity of 1,5-ribulose bisphosphate (RuBP) carboxylase, an enzyme that catalyzes CO_2 fixation during photosynthesis, can be inhibited by O_3. For example, 0.12 ppm for 2 hours inhibited the activity of RuBP carboxylase in rice (Nakamura and Saka, 1978). Inhibition of RuBP carboxylase activity is a relatively early event occurring several hours after conclusion of the O_3 exposure. Pell and Pearson (1983) observed 36, 68, and 80 percent decreases, respectively, in the concentration of 1,5-RuBP carboxylase in foliage of three alfalfa cultivars that had been exposed to an O_3 concentration of 0.25 ppm for 2 hours. Observations were made 48 hours after exposure on leaves that did not exhibit macroscopic injury symptoms. Crystals observed ultrastructurally in the chloroplast stroma of beans and hybrid poplars exposed to O_3 were thought to be 1,5-RuBP carboxylase (Thomson, 1975; Noble et al., 1980).

In some of the studies cited above, researchers examined the specific effects of O_3 on key steps in photosynthesis. The effect of O_3 on apparent photosynthesis, a measure of CO_2 uptake or fixation or both, was measured for many more plant species (Table 6-1). Reductions in apparent photosynthesis may reflect the direct impairment of chloroplast function or reduced CO_2 uptake resulting from O_3-induced stomatal closure, or both. Regardless of the mechanism, a sustained reduction in photosynthesis will ultimately affect the growth, yield, and vigor of the plant.

When considering dose-response effects of O_3 on plant yield in this document, emphasis has been placed on studies in which O_3 concentrations of 0.25 ppm or below were utilized (Table 6-1). Examples of O_3-induced reduction in apparent photosynthesis at concentrations exceeding 0.25 ppm are also presented (Table 6-1). These data highlight the potential of O_3 to reduce primary

TABLE 6-1. EFFECT OF OZONE ON PHOTOSYNTHESIS

Species	O_3 concentration, ppm[a]	Exposure duration	% inhibition	Reference
Loblolly pine	0.05	18 wk continuously	15[b]	Barnes (1972a)
Slash pine	0.05	18 wk continuously	9[b]	Barnes (1972a)
Bean	0.072	4 hr/day for 18 days	18[b]	Coyne and Bingham (1978)
Alfalfa	0.10	1 hr	4[b]	Bennett and Hill (1974)
	0.20	1 hr	10[b]	
Ponderosa pine	0.15	9 hr daily/ 60 days	25[c]	Miller et al. (1969)
	0.30	9 hr daily/ 30 days	67[c]	
Eastern white pine	0.15	19 days	10[c]	Barnes (1972a)
Eastern white pine	0.10	4 hr/day for 50 days	24[b]	Yang et al. (1983)
Sensitive	0.20	4 hr/day for 50 days	42[b]	
	0.30	4 hr/day for 50 days	51[b]	
Intermediate	0.10	4 hr/day for 50 days	Not sig. different	
	0.20	4 hr daily/50 days	14[b]	
	0.30	4 hr daily/50 days	20[b]	
Bean	0.30	3 hr	22[c]	Pell and Brennan (1973)
Black oak	0.50	4 hr daily/2 days	30 ± 10[d]	Carlson (1979)
Sugar maple	0.50	4 hr daily/2 days	21 ± 10[d]	Carlson (1979)
White pine				
Sensitive	0.7 or 0.9	3.0 or 10	100[b]	Botkin et al. (1972)
Tolerant	0.70 to 0.95	10/30 days	0[b]	
Poplar hybrid	0.90	1.5 hr	60[e]	Furukawa and Kadota (1975)
Ponderosa pine	450, 700 800 ppm-hr	Cumulative dose over 1,2,3 yr	90[b]	Coyne and Bingham (1981)

[a] 1 ppm = 1960 µg/m.

[b] $P < 0.05$.

[c] $P < 0.01$.

[d] Standard deviation.

[e] No statistical information.

productivity. Several of the studies provide data more pertinent to the ambient atmosphere. Barnes (1972a) examined the impact of O_3 on seedlings of three species of pine at concentrations of 0.05 or 0.15 ppm continuously for 19 days to 18 weeks. In younger seedlings of eastern white pine, which bore only primary needles, O_3 had little influence on photosynthetic rate. In older seedlings with secondary needles, photosynthesis was slightly depressed. With seedlings of slash, eastern white, and loblolly pines, exposure at 0.15 ppm O_3 had a relatively consistent depressing influence on photosynthesis of all species. At 0.05 ppm, however, O_3 appeared to stimulate photosynthesis in older secondary needles and depress photosynthesis in younger secondary needles. Barnes (1972a,b) used a Mast meter to measure O_3; the Mast meter can underestimate the O_3 concentration unless it is calibrated against a reference standard (Chapter 4). Also, the sample size used in these experiments was very small, four to nine seedlings. It is possible that variation among samples may have masked potential effects in some of the experiments (Barnes, 1972a). Coyne and Bingham (1978) exposed field-grown snap beans to an O_3 concentration of 0.072 ppm (the O_3 monitor was calibrated by UV photometry; see Chapter 4) for 4 hours per day for 18 days. Apparent photosynthesis was reduced 18 percent in plants treated with O_3. Bennett and Hill (1974) reported that apparent photosynthesis of alfalfa plants was depressed 4 percent and 10 percent when O_3 concentrations were 0.1 and 0.2 ppm for 1 hour, respectively. Methods of O_3 monitoring and calibration were not given by the authors.

Black et al. (1982) found a significant ($p < 0.001$) relationship ($r = -0.8$) between net photosynthetic rate of broad bean and 4-hour exposures to concentrations of O_3 0.05 to 0.30 ppm. Exposure to O_3 concentrations of less than 0.10 ppm resulted in a reversible depression of photosynthesis. Twenty hours after exposure to O_3 concentrations of 0.10, 0.20, and 0.30 ppm, photosynthetic rate was depressed by 0.04, 0.59 and 1.14 g CO_2/m^2 per hour, respectively, when compared with an initial rate of approximately 2.10 g CO_2/m^2 per hour (based on values presented for one example in the study). Miller et al. (1969) found that 3-year-old ponderosa pine seedlings sustained a 25 percent reduction in apparent photosynthesis after a 60-day exposure to an O_3 concentration of 0.15 ppm for 9 hours per day. Yang et al. (1983) exposed three clones of white pine, classified by foliar response to O_3 as sensitive, intermediate, and insensitive, to O_3 concentrations of 0.10, 0.20, or 0.30 ppm for 4 hours per day for 50 days in CSTR chambers. Net photosynthesis was reduced in the foliage of sensitive and intermediate clones by 14 to 51 percent in direct relation to O_3 dose and relative clonal sensitivity (Table 6-1). In another study, Coyne and Bingham (1981) measured changes in gross photosynthesis in needles of ponderosa pine trees of various sensitivities to O_3. Needles sustaining slight, moderate, and severe injury exhibited a 90 percent reduction in gross photosynthesis after exposure to a dose of 800, 700, and 450 ppm-hours O_3, respectively, in a 3-year time period (2 years for the most sensitive class of trees). The percentage inhibition in gross photosynthesis was based on photosynthetic rates of newly emerged needles; no true controls were used in the experiment. The authors emphasized that the decline in photosynthesis reflected the superimposition of O_3 effects on normal aging.

6.3.1.5 Tissue and Organ Responses. In addition to depressing photosynthesis in the foliage of many plant species, O_3 inhibits the allocation and translocation of photosynthate (e.g., sucrose) from the shoots to the roots and other organs (Tingey, 1974; Jacobson, 1982). Tingey et al. (1971a) found that when radish plants were exposed to O_3 (0.05 ppm for 8 hours, 5 days per week for 5 weeks), hypocotyl growth was inhibited 50 percent, while foliage growth was inhibited only 10 percent (both significant at $p < 0.01$). Walmsley et al. (1980) confirmed that radish plants exposed to O_3 (0.17 ppm continuously for 36 days) exhibited an altered pattern of assimilation such that below-ground biomass was more severely affected than foliage. Ponderosa pine exposed to 0.10 ppm O_3 for 6 hours per day for 20 weeks stored significantly less sugar and starch in their roots compared to control plants (Tingey et al., 1976a). Such an effect on translocation could reduce root weight and directly affect the yield of a crop like radish or carrot.

Snap beans exposed to O_3 (0.30 ppm or 0.60 ppm for 1.5 hours) exhibited a greater reduction in root than shoot growth (Blum and Heck, 1980). The root-to-shoot ratio of crimson clover was suppressed 17 percent and 23 percent, respectively ($p < 0.05$), when plants were exposed to O_3 at 0.03 and 0.09 ppm for 8 hours per day for 6 weeks (Bennett and Runneckles, 1977). The root-to-shoot ratio of rye grass was reduced 22 percent ($p < 0.05$) when plants were exposed to 0.09 ppm with the same exposure regime. In other experiments, the effects of O_3 were measured on the partitioning of photosynthate in carrot, parsley, sweet corn, cotton, and pepper (Oshima, 1973; Bennett and Oshima, 1976; Oshima et al., 1978; Oshima et al., 1979; Bennett et al., 1979). In each of these experiments, plants were exposed to O_3 concentrations of 0.12 to 0.25 ppm for 3 to 6 hours for 0.2 percent to 7 percent of the total growth period of the plants. In all species but pepper, root dry weight was depressed much more than leaf dry weight. For example, root dry weight of cotton was reduced 60 percent, whereas leaf dry weight was depressed only 17 percent by O_3 (Oshima et al., 1979). Ozone had virtually no effect on the dry weight of parsley leaves, but it reduced root dry weight 43 percent (Oshima et al., 1978). The photosynthetic rate of tomato plants exposed to O_3 (0.3 ppm for 3 hours) was reduced 35 percent and the translocation of photosynthate from the leaves was reduced 29 percent (McCool and Menge, 1983). This combined reduction in photosynthate available for root growth can significantly affect plant growth. The reduction in photosynthate translocation to roots and the resulting decrease in root size indicates that the plant had fewer stored reserves, rendering it more sensitive to injury from cold, heat, or water stress.

When less carbohydrate is present in roots, less energy will be available for root-related functions. In the 1978 criteria document (U.S. Environmental Protection Agency, 1978), evidence was presented for O_3-induced reduction in nodulation and nitrogen fixation in soybean and ladino clover. Blum and Tingey (1977) reported that when 2-week-old soybean plants were exposed to an O_3 concentration of 0.50 ppm for 4 hours, nodulation was inhibited 60 percent ($p < 0.05$). Ensing and Hofstra (1982) measured nitrogenase activity in the roots of red clover 1 and 6 days after the plants were exposed to O_3 (0.20 ppm 16 hours per day for 4 days) in non-filtered open-top chambers and found that nitrogenase activity was reduced 50 and 24 percent ($p = 0.05$), respectively, when compared to the activity in plants growing in charcoal-filtered open-top chambers. By 16 days post-exposure, enzyme activity was comparable to that in plants given other treatments. An ozone-induced suppression of atmospheric nitrogen fixation by root nodules could affect total biomass and agricultural yield, especially in areas where soil nitrogen is low.

6.3.1.6 Secondary Metabolic Responses. In addition to the physiological effects more directly related to productivity, there are many secondary metabolic responses in a plant exposed to O_3. While these responses do not explain the initial reaction to O_3, they may contribute to the manifestation of foliar injury. Ethylene is an important stress metabolite produced by many plants exposed to O_3 (Tingey, 1980). Ozone at 0.15 ppm for 8 hours increased ethylene evolution in beans (Stan et al., 1981). Ozone-enhanced ethylene evolution ceased prior to the appearance of visible injury. It has been proposed that ethylene may initiate the observed stimulation of oxidizing enzymes such as phenylalanine lyase, polyphenoloxidase, and peroxidase (Tingey et al., 1975).

The accumulation of phenols has been observed in many plant species in response to O_3 (Howell and Kremer, 1973; Hurwitz et al., 1979; Keen and Taylor, 1975; Koukol and Dugger, 1967). There appears to be a direct relationship between the concentration of phenols detected in foliage and the extent of visible injury induced by O_3 (Hurwitz et al., 1979). The pigmented lesions that are visible in the leaf following O_3 exposure are thought to occur when phenols are oxidized and polymerized (Howell and Kremer, 1973).

In summary, ozone enters the cell and initiates biochemical and physiological responses. Critical effects, including reduction in photosynthesis and a shift in the assimilation of photosynthate, will lead to reduced biomass, growth, and yield. Visible injury, which results from O_3-induced cell injury and death, reflects the occurrence of both primary and secondary metabolic events. Visible injury serves as an indicator of the presence of O_3 and reflects potentially harmful effects on plant vigor.

6.3.2 Factors that Modify Plant Response

There is a great deal of variation in the magnitude of plant response to O_3. Biological, physical, and chemical variables influence plant response. For example, trees in a stand of ponderosa pine will not respond equally to exposure to O_3 because of genetic diversity in the sensitivity of individual trees and because of environmental heterogeneity in the habitat. Plants at different ages or at different temperatures, humidities, light intensities, or soil moisture regimes will respond differently to an equivalent O_3 exposure. The presence of several pollutants, chemical sprays, and biological pests all will contribute to determining the magnitude of plant response to O_3. In developing an understanding of O_3 effects, it is important to consider the O_3 sensitivity of the plant and the environmental conditions it is likely to experience during exposure. It is equally important to recognize that plants at certain stages of development or under a given set of environmental conditions may be differentially sensitive to O_3. In the subsequent discussion, the factors that modify plant response are grouped into three categories: biological, physical, and chemical factors.

6.3.2.1 Biological Factors

6.3.2.1.1 Genetic Factors. The genetic complement of a plant determines its potential response to O_3. Genetically controlled variation in response to O_3 has been observed among species, cultivars, and individuals within a population. Inherited variation in plant response to O_3 can be measured by using many plant response variables. Most researchers have investigated relative O_3 sensitivity by measuring foliar injury. Genetically controlled differences in response to O_3, however, are also reflected in differential yield and physiological effects, as well. A list of the plant species studied that exhibited differential ozone sensitivity within a species is presented in Appendix B.

The relative O_3 sensitivity of cultivars within a species can vary with dose and the nature of the response measured (Tingey et al., 1972; Heagle, 1979b). There may also be some disparity between the relative sensitivity ranking of cultivars from controlled O_3 exposures in a laboratory and exposure of the same cultivars to ambient air oxidants in the field (Engle and Gabelman, 1966; Taylor; 1974; Huang et al., 1975; Meiners and Heggestad, 1979; Hucl and Beyersdorf, 1982; DeVos et al., 1983). The inconsistent results may be explained in part by the nature of the inheritance of the O_3 sensitivity. In the case of onion and bean, one or a few gene pairs were associated with O_3 sensitivity (Engle and Gabelman, 1966; Butler et al., 1979); while for corn (Cameron, 1975), tobacco (Povilaitis, 1967; Sung et al., 1971; Aycock, 1972; Huang et al., 1975), potato (DeVos et al., 1982) and petunia (Hanson et al., 1976), several genes determine plant responses to O_3. The apparent genetic complexity explains the potential variability in plant response as gene expression changes during plant development and with variations in the environment.

In agricultural ecosystems there may be some inadvertent selection for breeding lines tolerant of ozone, as the plant breeder frequently selects for those plants that perform best under the local growing conditions. There is no documentation, however, that such inadvertent selection is occurring. In natural ecosystems in areas receiving long-term O_3 stress, it is postulated that sensitive individuals within a population may decline and be replaced by those more tolerant to the pollutant (see Chapter 7). Many stresses, including SO_2, elicit this kind of response in populations in natural ecosystems (Taylor and Murdy, 1975; Roose et al., 1982). Narrowing of the gene pool creates the potential for increased vulnerability of a plant population to various assaults, including those of biotic pests.

It appears that as wide a range of sensitivity to O_3 exists among plant species as within them. Ozone is prevalent in most agricultural regions in the United States. Sensitive plant species are found throughout the country and the environmental conditions that favor injury occur in many geographic locations.

6.3.2.1.2 Developmental factors. Plant foliage appears to be most sensitive to O_3 just prior to or at maximum leaf expansion (U.S. Environmental Protection Agency, 1978). At this stage, stomata are functional, intercellular spaces are expanded, and barriers to gas exchange such as internal cutin and secondary thickening of cell walls are minimal (U.S. Environmental Protection Agency, 1978). Blum and Heck (1980) analyzed the response of bean plants to O_3 concentrations of 0.30 and 0.60 ppm for 1.5 hours at various stages during growth. The plants were most sensitive to O_3 early in development and just before senescence. Virginia pine and petunia seem to be most sensitive to O_3 early in development, as described in the 1978 criteria document (U.S. Environmental Protection Agency, 1978). Tolerance of foliage to O_3 increased at or just before appearance of flower buds in plants from six F_1 hybrid multiflora petunia lines, at eight physiological ages, that were exposed to O_3 (0.20 ppm for 8 hours) (Hanson et al., 1975). The effect of O_3 on root dry weight of radish was related to timing of the exposure (Tingey et al., 1973a). Plants exposed to an O_3 concentration of 0.40 ppm for 1.5 hours at 7, 14, or 21 days from seeding, sustained 25, 37, and 15 percent ($p < 0.05$) inhibition of hypocotyl root dry weight, respectively. Radish plants may be particularly sensitive to O_3 at 14 days because maximum root enlargement begins at that time.

One of the first observations of the effects of photochemical oxidants on plants in the field was the development of leaf chlorosis followed by premature leaf aging (senescence) and early leaf drop (abscission) (e.g., Richards et al., 1958; Menser and Street, 1962). Ozone (0.05 or 0.10 ppm 6 hours per day for 133 days) induced premature leaf drop in soybeans (Heagle et al., 1974). The premature senescence and leaf drop increased throughout the study period. Ozone-induced premature leaf senescence has been observed in both greenhouse and field-grown potatoes (Heggestad, 1973; Pell et al., 1980). Field studies with white beans (Hofstra et al., 1978) confirmed that premature leaf drop was induced by O_3; the premature leaf drop was associated, in part, with the O_3-induced yield reductions. The photosynthetic rate of hybrid poplars exposed to O_3 (0.085 or 0.125 ppm for 5.5 hours per day for 65 days) decreased more rapidly with age than unexposed plants, indicating that O_3 induced a premature senescence (Reich, 1983). Another study with hybrid poplar showed that O_3 (0.04 ppm 12 hours per day for 5 months) significantly increased leaf drop (Mooi, 1980). The effects of O_3 on the senescence process, regardless of time of initiation, may be responsible for many of the documented reductions in yield.

6.3.2.1.3 Pollutant-plant-pest interactions. Plant pests (pathogens and insects) are normal components of both agro- and natural ecosystems. Crop losses from pests can be significant and have been estimated at 20 to 30 billion dollars per year in the United States alone (James, 1980). When considering the effects of O_3 on crop plants or forests, it is important to realize that the pollutant does not occur alone, but rather in conjunction with other stresses that are modifying the productivity of the system. The purpose of this section is to indicate what is known about interactions among O_3, plants, and pests, and how these interactions might modify the effects of O_3 on the quality, quantity, or the intended use of the plant.

Disease is the result of a complex interaction between host plant, environment, and pathogen. In the context of this general discussion of biotic stress, problems caused by pathogens and insects will both be termed disease. To understand the ways in which O_3, as a part of the environment, may modify pest dynamics, it will be helpful to consider a generalized disease cycle.

The cycle begins with the arrival of the inoculum or pest at the plant (host). Following deposition of the pest on the plant surface, in the presence of favorable conditions (temperature, moisture), penetration of the plant (or insect feeding, or oviposition) may begin.

Host penetration may occur quickly or, in some cases, the pathogen may live as a resident on the plant surface for a period of time. Once penetration occurs, and favorable conditions are present, infection may occur that results in an intimate relationship between plant and pathogen. Growth and development or colonization by the pathogen or plant pest proceeds until the pest reaches a reproductive stage. Propagules of the pest are formed and dispersed either passively or actively.

At each stage of this cycle, O_3 may modify the success of the pest, either directly through effects on the invading organisms, or indirectly, through modification of the host plant. Similarly, the complex interaction between plant and pest may alter the sensitivity of the plant to O_3.

6.3.2.1.3.1 Pollutant-plant-pathogen interactions. Most pollutant-plant-pathogen interaction studies have been conducted under controlled laboratory conditions, but a few field studies have been performed. This topic has been reviewed recently (Heagle, 1973, 1982; Laurence, 1981; Manning, 1975; Treshow, 1980a; U.S. Environmental Protection Agency, 1978). The results of published studies are summarized in Table 6-2.

TABLE 6-2. PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS DOSES OF OZONE UNDER LABORATORY AND FIELD CONDITIONS

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b,c]	Reference
AGRONOMIC CROP/FUNGI					
Pinto bean/root fungi	0.10 ppm O_3, 8 hr daily, 10 wk	L	Increased number fungal colonies	NR	Manning et al. (1971)
Barley/*Erysiphe graminis*	0.15 ppm O_3, 6 hr daily for 4, 6, or 8 exposures after inoculation	L	Increased colony size	NR	Heagle and Strickland (1972)
Wheat/*Puccinia graminis*	0.06 to 0.18 ppm O_3, 6 hr daily, 17 days after inoculation	L	Decreased hyphal growth, numbers of spores, infection	Decreased	Heagle and Key (1973a)
Wheat/*Puccinia graminis*	0.1 ppm O_3, 6 hr daily, 12 days after inoculation	L	Reduced sporulation	NR	Heagle (1975)
Corn/*Helminthosporium maydis*	0.06 to 0.18 ppm O_3 6 hr variable days before and after inoculation	L	Increased lesion size, increased number of spores produced at highest concentration	NR	Heagle (1977)
Oats/*Puccinia coronata*	0.10 ppm O_3, 6 hr/day 10 days after inoculation 0.20 ppm O_3/3 hr, 1 to 5 days after inoculation	L	No effect on disease development	NR	Heagle (1970)
Potato/*Botrytis cinerea*	0.15 to 0.25 ppm O_3, 6 to 8 hr	L	Increased disease development	NR	Manning et al. (1969)
Cabbage/*Fusarium oxysporium*	0.10 ppm O_3, 8 hr daily, 10 wk	L	Decreased disease development	NR	Manning et al. (1971a)
Onion/*Botrytis cinerea*, *B. squamosa*	0.15 ppm O_3, 4 hr	FC	Increased disease development	NR	Wukasch and Hofstra (1977a,b)
Potato/*Alternaria solani*	0.03 to 0.04 ppm O_3 monthly	F	Increased disease development	NR	Bisessar (1982)
Tomato/*Glomus fasciculatus*	0.30 or 0.60 ppm, 3 hr/wk for 8 wks	L	Retarded infection	NR	McCool et al. (1982)

TABLE 6-2 (cont'd). PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS DOSES OF OZONE UNDER LABORATORY AND FIELD CONDITIONS

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b,c]	Reference
TREES AND ORNAMENTALS/FUNGI					
White pine/*Lophodermium pinastri*	0.07 ppm O_3, 4.5 hr	L	Slight increased disease occurrence	NR	Costonis and Sinclair (1972)
Ponderosa, Jeffrey Pine/*Heterobasidion annosum*	0.18 ppm O_3/12 hr seasonal	F	Increased disease development Increased colonization of stumps	NR NR	James et al. (1980a) James et al. (1980b)
Eastern white pine/*Verticicladiella procera*	0.045 ppm O_3 monthly average 0.128 ppm monthly peak hourly	F	Increased disease incidence	NR	Skelly (1980)
Lilac/*Microsphaera alni*	0.25 ppm O_3, 72 hr	L	No influence on germination, early fungal development	NR	Hibben and Taylor (1975)
Poinsettia/*Botrytis cinerea*	0.15 to 0.45 ppm O_3, 4 hr	L	No effect	NR	Manning et al. (1972)
Geranium/*Botrytis cinerea*	0.15 ppm O_3, 6 hr, 2x at 24-hr intervals after inoculation	L	Reduced sporulation; reduced infection by exposed spores Flocculent material produced	NR	Krause and Weidensaul (1978a)
Geranium/*Botrytis cinerea*	0.07 to 0.10 ppm O_3 10 hr daily for 15 to 30 days	L	Increased disease development when visible O_3 injury evident	NR	Manning et al. (1970b)
Citrus/*Glomus fasciculatus*	0.45 ppm 3 hr/day, 2 days/wk for 19 wks	L	Decreased infection	NR	McCool et al. (1979)

TABLE 6-2 (cont'd). PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS DOSES OF OZONE UNDER LABORATORY AND FIELD CONDITIONS

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b,c]	Reference
AGRONOMIC CROPS/VIRUS					
Tobacco/tobacco mosaic	0.30 ppm O_3, 6 hr Seasonal maximum hour, 0.236 ppm O_3	L F	NR	< O_3 injury < O_3 injury	Brennan and Leone (1969) Bisessar and Temple (1977)
Tobacco/tobacco etch	0.25 ppm O_3, 4 hr, once 9 days after inoculation	L	NR	< O_3 injury	Moyer and Smith (1975)
Tobacco/tobacco streak	0.30 ppm O_3, 3 hr for 1 or 2 days	L	NR	> O_3 injury	Reinert and Gooding (1978)
Tobacco-pinto bean/tobacco mosaic	0.35 ppm O_3, 4 hr; 0.25 ppm O_3, 3 hr, respectively	L	NR	< O_3 injury	Brennan (1975)
Pinto bean/bean common mosaic	0.25 ppm O_3, 4 hr, 5 days after inoculation	L	NR	< O_3 injury	Davis and Smith (1975)
Pinto bean/alfalfa mosaic, tobacco ringspot, tobacco mosaic, tobacco ringspot	0.25 ppm O_3 4 hr, 5 days after inoculation		NR	< O_3 injury	Davis and Smith (1976)
Tomato/tobacco mosaic, cucumber mosaic	0.0 to 0.45 ppm or 0 to 0.90 ppm 3 hr; 7 to 21 days after inoculation	L	NR	> O_3 injury at 7 or 14 days < O_3 injury at 21 days	Ormrod and Kemp (1979)
Soybean/tobacco ringspot	0.35 to 0.40 ppm O_3, 4 hr, once 6, 8, or 10 days before inoculation	L	NR	< O_3 injury	Vargo et al. (1978)

TABLE 6-2 (cont'd). PLANT AND BIOTIC PATHOGEN INTERACTIONS AS INFLUENCED BY VARIOUS DOSES OF OZONE UNDER LABORATORY AND FIELD CONDITIONS

Plant/pathogen	Exposure	Experimental conditions[a]	Effect on disease	Effect on pollutant injury[b,c]	Reference
AGRONOMIC CROP/BACTERIA					
Alfalfa/*Xanthomonas alfalfae*	0.20 ppm O_3, 4 hr at 24 hr before or after O_3 exposure	L	Reduced disease development	< O_3 injury	Howell and Graham (1977)
White bean/*Xanthomonas phaseoli*	0.08 ppm O_3, 11 hr average, seasonal	F	No effect	< O_3 injury	Temple and Bisessar (1979)
Soybean/*Pseudomonas glycinea*	0.08, 0.25 ppm O_3, 4 hr	L	Reduced disease incidence	No effect	Laurence and Wood (1978a)
Ladino clover/*Rhizobium* sp.	0.30 to 0.60 ppm O_3, 2 times to 2 hr	L	Reduced nodule number		Letchworth and Blum (1977)
Soybean/*Rhizobium japonicum*	0.75 ppm O_3, 1 hr	L	Reduced growth and nodulation	No effect	Tingey and Blum (1973)
Wild strawberry/*Xanthomonas fragariae*	0.20 ppm O_3, 3 hr before or after inoculation 0.08 ppm (as above)		Reduced disease incidence Inconsistent results	No effect	Laurence and Wood (1978b)
NEMATODES					
Soybean/cyst, stubby root	0.25 ppm O_3, 4 hr/4 days before inoculation. 3 days/wk for 4 hr/day after inoculation until harvest	L	Reduced reproduction of nematode		Weber et al. (1979)
Begonia/foliar	0.25 ppm O_3, 4 hr at 3 days before or after inoculation	L	Reduced reproduction of nematode		Weber et al. (1979)

[a] L = Laboratory, greenhouse, growth, or fumigation chamber studies; F = field studies; FC = chambers used in field studies.

[b] > = Increased; < = decreased.

[c] NR = Not reported.

Source: Modified from Laurence (1981).

Infection of plants by pathogens may be inhibited or stimulated by O_3. Manning et al. (1969; 1970a,b) found that potato and geranium leaves injured by O_3 (0.07 to 0.25 ppm, 6 to 10 hours) had a larger number of lesions caused by Botrytis. Wukasch and Hofstra (1977a) found that field-grown O_3-injured onion plants developed twice as many Botrytis squamosa lesions as did uninjured plants growing in charcoal-filtered air. The same authors (1977b) found fewer natural B. squamosa lesions on plants that had been treated with an antioxidant chemical having no fungicidal activity. Ambient air O_3 concentrations exceeded 0.15 ppm for 4 hours and 0.08 ppm on several occasions during the growing season. Bisessar (1982) found similar results with the interaction of O_3, potato, and Alternaria solani. The fungus colonized O_3-injured sites on potato leaves, and fewer lesions were present on plants protected from O_3 with ethylene diurea (EDU), a compound developed to reduce O_3 injury (see Section 6.3.2.3.2). Ambient air O_3 concentrations exceeded 0.08 ppm during 68 hours, and the highest measured concentration was about 0.14 ppm. Similar results were obtained by James et al. (1980a) in a field study of Heterobasidion annosum (syn. Fomes annosus) infection of oxidant-injured ponderosa and Jeffrey pines in the San Bernardino Mountains. They found increased infection of the roots of severely O_3-injured trees. The results of the field study were confirmed under controlled laboratory conditions. They also found that the colonization of roots and freshly cut stumps of ponderosa and Jeffrey pine was positively correlated with the severity of the oxidant injury observed on needles. In laboratory studies, colonization of both species was directly related to O_3 exposure over the range of 0 to 0.45 ppm for 58 to 92 days (see discussion in Chapter 7). Skelly (1980) reported increased incidence of root disease caused by Verticicladiella procera in oxidant-injured eastern white pines in Virginia.

Ozone can inhibit infection of plants by pathogens. In general, infection by obligate parasites is inhibited in plants that have been exposed to elevated concentrations of O_3 (Heagle 1970, 1973, 1975, 1982; Heagle and Strickland, 1972; Heagle and Key, 1973a,b).

McCool et al. (1979) reported that infection of citrus by Glomus fasciculatus, an endomycorrhizal fungus, was decreased by exposure to O_3 (0.45 ppm, 3 hours per day, 2 days per week for 19 weeks). Exposure of tomato to 0.30 ppm O_3 for 3 hours once weekly for 8 weeks retarded infection by the same fungus (McCool et al., 1982). These exposures did not affect root growth of the plants or sporulation by the fungus, but did reduce the number of successful infections. Ozone reduced mycorrhizal infections of tomato roots 46 and 63 percent when the plants were exposed to 0.15 (3 hours per exposure, twice weekly for 9 weeks) or 0.30 ppm (3 hours once weekly for 9 weeks), respectively. Rhizobium, a nitrogen-fixing bacterium of legumes, induced fewer nodules in soybean plants exposed to 0.75 ppm O_3 for 1 hour (Tingey and Blum, 1973) and in ladino clover exposed to 0.3 or 0.6 ppm O_3 twice for 2 hours each (Letchworth and Blum, 1977).

Infection of soybean by Pseudomonas glycinea was decreased when plants were exposed to 0.08 or 0.25 ppm O_3 for 4 hours at times ranging from 8 days to 1 hour before inoculation. When exposures occurred more than one day after inoculation, however, inhibition was not observed (Laurence and Wood, 1978a). Similar results were found with Xanthomonas fragariae and wild strawberry (Fragaria virginiana) (Laurence and Wood, 1978b). Temple and Bisessar (1979), however, did not find fewer Xanthomonas phaseoli lesions on O_3-injured white beans in the field.

In most cases, colonization of plant tissue by pathogens is assessed by measuring lesion size. Lesions of obligate parasites are usually smaller on plants exposed to O_3 when compared to controls (Laurence, 1981). Heagle and Strickland (1972), however, found larger colonies of Erysiphe graminis f. sp. hordei on barley plants that were exposed repeatedly to low concentrations of O_3 (up to 0.15 ppm, 6 hours per day for 8 days).

Little is known about colonization of ozone-affected plants by facultative parasites. Heagle (1977) inoculated corn plants with Helminthosporium maydis race T and exposed them to O_3 (0.06, 0.12, or 0.18 ppm) for 6 hours per day for up to 7 days before inoculation, 9 days after inoculation, or combinations of before and after. He found that lesion length was significantly increased by O_3 exposure (0.18 ppm) before and after inoculation, but was not affected at other concentrations or time regimes.

Based on these few reports on the relationship of O_3 to plant colonization by pathogens, it is impossible to generalize and predict effects in particular disease situations. It is apparent that the outcome of a pollutant-plant-pathogen interaction depends on the particular plant and pathogen involved. It also is affected by the environmental conditions and O_3 concentrations before and after inoculation.

Rist and Lorbeer (1981) recently reviewed the effects of O_3 on sporulation of fungi. In axenic culture, sporulation and growth of fungi isolated from leaf surfaces were almost always inhibited or unchanged by exposure to O_3. In a few studies, significant inhibition of growth, sporulation, or germination has been observed following exposures to concentrations as low as 0.10 ppm for 4 hours, but fungi often are resistant to 1.0 ppm O_3 for several hours. Germination of spores produced during O_3 exposure (0.15 or 0.30 ppm, 6 hours per day for 2 days) may also be lower than that of controls (Krause and Weidensaul, 1978a,b). These spores may subsequently be less successful in colonizing the leaf surface (Krause and Weidensaul, 1978a,b). Both decreases and increases in sporulation have resulted from O_3 exposure of infected plants (Laurence, 1981), and the particular result seems to depend on the plant-pathogen combination and the specific O_3 exposure regime.

In the case of bacterial diseases, reproduction of the pathogen is generally reflected in the size of lesions on the plant. Bacteria are generally resistant to ambient concentrations of O_3, but may be much more sensitive to changes in plant metabolism induced by O_3 (Hughes and Laurence, 1984).

Reproduction of the soybean cyst nematode and the stubby root nematode was reduced by exposure of infested soybean plants to 0.25 ppm O_3 applied on three alternate days a week for about 2 months (Weber et al., 1979). Similar O_3 treatments also reduced the reproduction of a foliar nematode on begonia plants. This reduction was related to the amount of O_3-induced leaf injury (Weber et al., 1979).

Only a few studies have been reported that relate the effects of O_3 in combination with another pollutant (SO_2) to disease development. Weidensaul and Darling (1979) found that Scotch pines inoculated with Scirrhia acicola and exposed to O_3 (0.20 ppm for 6 hours) or O_3 combined with SO_2 (0.20 ppm each for 6 hours) had fewer lesions than controls, but did not differ from each other. More lesions formed when inoculation preceded fumigation by 5 days than when inoculation followed exposure by 30 minutes.

6.3.2.1.3.2 Effects of ozone on plant-insect interactions. The effects of air pollutants on insect populations were reviewed recently (Alstad et al., 1982). Very little is known about O_3-insect interactions. Ozone-induced injury in ponderosa pine has been shown to predispose trees to subsequent invasion by several species of pine bark beetles (Stark et al., 1968). Elden et al. (1978) found that O_3 injury induced by exposures of 0.20 ppm for 4 hours had little or no effect on the development of pea aphids on alfalfa. They did note that two of three varieties having higher degrees of O_3 resistance also had greater resistance to pea aphid.

6.3.2.1.3.3 Effects of pathogen infection on plant sensitivity to O_3. Fungal, bacterial, or viral infections have been reported to provide some protection to plants from the visible effects of O_3. Although of interest mechanistically, most of the studies have been conducted under controlled conditions, and it is questionable whether they are relevant in field situations.

Yarwood and Middleton (1954) noted that pinto bean leaves infected by *Uromyces phaseoli* were less sensitive to photochemical oxidants than uninfected leaves. Similar results have been observed with many pathogen-plant combinations. The protection afforded by fungal and bacterial pathogens is usually localized at the margins of lesions, while virus infections can provide more generalized effects (Heagle, 1982).

Although bacterial pathogens often provide protection against O_3 injury near lesions, they did not in the case of bacterial blight of soybean or angular leafspot of strawberry (Laurence and Wood, 1978a,b). Pratt and Krupa (1979), however, reported that in chlorotic soybean leaves *Pseudomonas glycinea* infection did inhibit expression of O_3 symptoms. Temple and Bisessar (1979) found less visible O_3 injury on *Xanthomonas phaseoli*-infected white beans in the field in Ontario, Canada. Using the same species of bacterium, Olson and Saettler (1979) observed no protection from O_3 injury in controlled laboratory experiments. Pell et al. (1977) investigated the interaction between O_3 and a species of *Pseudomonas* that caused a hypersensitive reaction in soybean. They found that inoculation with the pathogen provided some protection from O_3 when plants were inoculated 1 day before exposures to a relatively high concentration of the pollutant (0.35 ppm for 2 hours). The effect was not observed when inoculation took place 4 hours before exposure.

Many reports have appeared on the effects of virus infection on plant response to O_3, beginning with those of Brennan and Leone (1969) and Brennan (1975). Davis and Smith (1975, 1976) reported protection of pinto bean leaves from O_3 injury following inoculation with common mosaic, tobacco ringspot, tomato ringspot, alfalfa mosaic, or tobacco mosaic viruses. The protection depended upon an establishment time of 4 to 5 days between inoculation and exposure, which was apparently linked to the time required to attain sufficient virus titer to afford protection. The protection was localized except in the case of tobacco ringspot, in which a more general effect was observed. Infection with tobacco etch virus also protected tobacco plants from O_3 injury

(Moyer and Smith, 1975). All experiments were under controlled conditions with exposures of 0.25 ppm O_3 for 4 hours.

Virus infection in one part of a plant has also been shown to provide protection against O_3 injury in other parts. Davis and Smith (1976) found that inoculation of one primary leaf of a pinto bean plant resulted in some degree of protection in the uninoculated leaf exposed to O_3 (0.20 ppm for 4 hours), but was not effective at O_3 concentrations greater than 0.20 ppm. Vargo et al. (1978) found that sensitivity to O_3 (0.35 to 0.4 ppm for 4 hours) of the primary leaf opposite the leaf inoculated with tobacco ringspot virus was decreased with increasing time after inoculation. They also found that as virus-induced apical necrosis increased, less foliar O_3 injury occurred.

Two reports show that O_3 injury may be increased following virus infection. Reinert and Gooding (1978) found that tobacco plants systemically infected with tobacco streak virus and exposed to O_3 (0.3 ppm for 3 hours on 1 or 2 days) 3 weeks after inoculation displayed more injury than the combined injury of plants exposed to O_3 or virus. Ormrod and Kemp (1979) found both increases and decreases in O_3 sensitivity of tomato plants infected with cucumber mosaic virus or tobacco mosaic virus or both, depending on the tomato cultivar, O_3 concentration, the virus, and the virus incubation period. Ozone injury was observed more frequently on tobacco mosaic virus-infected plants than on those inoculated with cucumber mosaic virus. They also observed that increases in O_3 injury usually occurred when O_3 exposures (0.15 to 0.90 ppm for 3 hours) occurred within 14 days of inoculation; 21 days after inoculation, most of the differences observed were decreases in injury.

In the only field study reported, Bisessar and Temple (1977) found 60 percent less oxidant injury on tobacco plants infected with tobacco mosaic virus than on uninfected plants. Ozone concentrations exceeded 0.10 ppm for 16 percent of the daylight (6:00 a.m. to 8:00 p.m.) hours during the study.

The effects described in the above sections are not of commercial importance, but the observations may provide some information as to the mode of action of O_3 in plants.

Ozone affects the development of disease in plant populations. Most laboratory evidence indicates that O_3, at ambient concentrations or higher for 4 hours or more, inhibits infection by pathogens and subsequent disease development; however, increases in disease development have been noted in certain cases. Most often these increases occur with "stress pathogens," such as Botrytis or Heterobasidion annosum, that incite diseases such as blight of potatoes or onions or root rot of ponderosa and Jeffrey pine. Increases in disease development have been observed in these host-parasite relationships under both laboratory and field conditions (plants exposed to ambient air levels of O_3).

That ozone can also modify plant-insect relationships is best illustrated by studies conducted in the San Bernardino Mountains that showed increased invasion of O_3-stressed pine trees by bark beetles.

The mode of action of O_3-plant-pest interaction probably involves indirect effects on the pathogen or insect that are the result of the direct interaction of O_3 and the plant. Effects on disease development have been documented at concentrations of O_3 and durations of exposure that are considered to be low (i.e., < 0.10 ppm for a few hours). Thus, it would appear that O_3 is affecting plant metabolism at these low concentrations and short exposure durations.

6.3.2.2 Physical Factors. The environment of the plant is composed of various biological, chemical, and physical factors that change throughout the plant growth period. The physical factors (e.g., light, temperature, relative humidity, soil moisture, and soil fertility) interact to provide the conditions for, and also govern, plant growth. Short-term variations in one or several of these environmental factors, if they coincide with a pollution episode, may render the plant more or less sensitive to pollutants.

Environmental conditions before and during plant exposure are critical to the plant response, while post-exposure conditions are less important. Although the influence of physical factors on plant response to O_3 has been studied primarily under laboratory and greenhouse conditions, field observations have often substantiated these results. Most studies have evaluated the effects of a single environmental factor and have usually used foliar injury as the measure of plant response. Information sufficient to make some generalizations about the influence of these factors on plant response to O_3 is available; but for most factors, substantial uncertainty exists because of the small number of species studied and the lack of information on the interactions of the environmental factors.

In this section, the various environmental factors will be discussed individually for organizational convenience, even though these factors interact to influence plant growth and sensitivity to O_3. Most studies in the following sections have used exposures to high O_3 concentrations that would rarely, if ever, be encountered in the ambient air. These studies were included because they illustrate the range of plant responses to various physical factors.

6.3.2.2.1 Light. It was concluded in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) that a short photoperiod and a relatively low light intensity during growth maximize O_3-induced foliar injury. These results were consistent across contrasting light regimes. For example, bean and tobacco plants were more sensitive to O_3 at 0.4 ppm for 1 hour if grown at 420 $\mu E\ s^{-1}\ m^{-2}$ than if grown at 840 $\mu E\ s^{-1}\ m^{-2}$ (Dunning and Heck, 1973). Cotton grown at 276 $\mu E\ s^{-1}\ m^{-2}$ was less sensitive to O_3 concentrations of 0.9 ppm for 1 hour than similar plants grown with 27.6 $\mu E\ s^{-1}\ m^{-2}$ (Ting and Dugger, 1968). Subsequently, Dunning and Heck (1977) demonstrated the complex nature of environmental interactions. They reported that tobacco showed increased sensitivity to an O_3 concentration of 0.40 ppm for 1 hour when grown under high light intensity (840 $\mu E\ s^{-1}\ m^{-2}$) and subsequently exposed at an intermediate light intensity (420 $\mu E\ s^{-1}\ m^{-2}$). In contrast, pinto bean leaves were most sensitive when plants were grown at a lower light intensity (209 $\mu E\ s^{-1}\ m^{-2}$) and subsequently exposed at the high intensities cited above.

In the field, vegetation will not often be exposed to O_3 at the low light intensities and the short photoperiods (8 hours) used in simulations described above. Therefore, special consideration of light may not be as relevant as other environmental factors. There are, however, some cultural practices for which light intensity and photoperiod are controlled. Shade-grown tobacco and bedding plants (in the commercial floriculture industry) represent two examples of production settings in which low light intensity is used and where losses attributable to oxidants have been documented.

6.3.2.2.2 Temperature. The 1978 criteria document (U.S. Environmental Protection Agency, 1978) reported that there was no consistent pattern relating temperature to plant response to O_3. Radish was more sensitive to O_3 if grown under cool conditions, whereas snap bean, soybean, Bel W-3 tobacco, Virginia pine, and white ash were sensitive if grown under warm conditions (U.S Environmental Protection Agency, 1978). Miller and Davis (1981a) found that pinto bean plants exposed to O_3 at a concentration of 0.10 ppm for 3 hours at 15° or 32°C sustained more severe foliar injury than when the exposure temperature was 24°C. Dunning and Heck (1977) also found that bean plants were more sensitive to O_3 when exposed at 16° or 32°C rather than at 21° or 27°C. Tobacco behaved differently from bean, exhibiting less sensitivity to 0.40 ppm O_3 for 1 hour when the exposure temperature was 32°C as opposed to 16°, 21°, or 27°C.

The effects of temperature on plant response to O_3 are probably both physical and biological. Temperature affects solubility of gases, enzymatic reactivity, membrane conformation, and stomatal movement. The disparate O_3 responses of various plant species grown at different temperature regimes may also reflect morphological or biochemical differences or both.

6.3.2.2.3 Relative humidity. It was concluded in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) that, in general, plants seem to be more sensitive to O_3 when growth or exposure, or both, occur under conditions of high relative humidity (RH). Table 6-3 is a modification of a summary table in the 1978 criteria document (U.S. Environmental Protection Agency, 1978). Dunning and Heck (1977) reported that the sensitivity of tobacco to O_3 (0.40 ppm for 1 hr) was not affected by the relative humidity during growth until the level reached 90 percent RH, at which point plants became more tolerant to O_3. McLaughlin and Taylor (1981) have demonstrated that, in pinto bean plants exposed to O_3 concentrations of 0.079 ppm for 2 hours, uptake of the pollutant increased fourfold when the exposure RH was increased from 35 percent to 73 percent. At the low RH (35 percent), O_3 uptake decreased when the pollutant concentration exceeded 0.079 ppm, while at the higher RH (73 percent) O_3 uptake increased with increasing O_3 concentration.

The influence of RH on stomatal function may help to explain the influence of RH and plant responses to O_3. As RH decreases, a water deficit can develop in the guard cells, and stomatal closure occurs to minimize internal foliar water deficit (Ludlow, 1980). Stomatal closure would reduce O_3 flux into the leaf. The influence of RH on plant sensitivity may explain important variations in plant response under field conditions.

6.3.2.2.4 Soil moisture. Plant response to oxidants is modified by soil moisture, probably through an influence on stomatal function. As soil moisture decreases, water stress increases and there is a reduction in plant sensitivity to O_3. In the previous criteria document (U.S. Environmental Protection Agency, 1978), the major studies on effects of soil moisture prior to 1978 were reviewed and examples are shown in Table 6-4. More recently, Harkov and Brennan (1980) demonstrated that potted hybrid poplar plants were more tolerant of O_3 concentrations of 0.10 ppm after 6 to 9 days without water. Olszyk and Tibbitts (1981) found that pea plants exposed to O_3 concentrations of 0.23 ppm for 2 hours exhibited less foliar injury when the plant water potential was -388 kPa than when it was -323 kPa (reflecting relatively low and high soil moisture levels, respectively).

TABLE 6-3. RESPONSE OF PLANTS TO OZONE AS CONDITIONED BY HUMIDITY DURING GROWTH AND EXPOSURE[a]

Plant species	Ozone concentration, ppm	Exposure duration, hr	Notes[b]	Growth or exposure[c]	Response, % injury[d]			
					60% RH	85% RH		
Pine, Virginia	0.25	4	3-yr seedlings	Exposure	4	25		
	0.25	4	Juvenile	Growth	50	58		
	0.25	4	Juvenile	Exposure	1	35		
					60% RH	80% RH		
Bean, cultivar Pinto	0.40	1	8 hr PP; 420 μE s^{-1} m^{-2} control conditions; 8 hr PP	Growth	66	78		
				Exposure	52	67		
					60% RH	80% RH		
Tobacco, cultivar Bel W_3	0.40	1	8 hr PP; 420 μE^{-1} m^{-2} control conditions, 8 hr PP	Growth	42	36		
				Exposure	33	36		
					60% RH	80% RH		
Ash, white	0.25	4	1-yr seedlings	Growth	33	46		
				Exposure	38	41		
				Post-exposure	36	41		
					26% RH	51% RH	95% RH	
Tobacco, cultivar Bel W_3	0.30	1.5	31°C	Exposure	9	39	50	
					26% RH	51% RH	95% RH	
Bean, cultivar Pinto	0.20	1.5	31°C	Exposure	0	0	55	
					45% RH	60% RH	75% RH	90% RH
Bean cultivar Pinto, and Tobacco, cultivar Bel W_3, averaged	0.40	1	8 hr PP	Growth				
				45% EH	36	39	41	31
				90% EH	73	67	81	80
			8 hr PP	Exposure 75% GH	41	53	70	81

[a] Modified from 1978 criteria document (U.S. Environmental Protection Agency, 1978); all the studies were conducted in controlled environment facilities.

[b] PP = photoperiod, GH = relative humidity during growth, EH = relative humidity during exposure.

[c] Time when humidity treatment was applied.

[d] Relative humidity levels during growth or exposure as indicated.

TABLE 6-4. EFFECTS OF SOIL MOISTURE ON RESPONSE OF SELECTED PLANTS TO OXIDANT

	Ozone exposure			Response, % reduction from control		
Plant species	Concentration, ppm	Duration	Type of response	High moisture[a]	Medium moisture[a]	Low moisture[a]
Tomato, cultivar Fireball				90% turgid	80% turgid	
	1.00	1.5 hr	Reduction in chlorophyll	54	10	
	1.00	1.0 hr	Reduction in chlorophyll	67	24	
	0.50	1.0 hr	Reduction in chlorophyll	36	(3)[b]	
	1.00	1.0 hr	Reduction leaf dry wt	48	(40)[b]	
Beet, garden	0.00	3 hr (daily for 38 days)		-40 kPa	-440 kPa	-840 kPa
	0.20		Reduction in dry wt of storage root from nonsaline control	0	24	68
				40	52	69
Bean, cultivar Pinto				-40 kPa	-200 kPa	-400 kPa
	0.00		Reduction in shoot dry wt from nonsaline control	0	18	78
	0.15	2 hr/day (63 days)		27	42	87
	0.25	2 hr/day (63 days)		93	91	88
	0.00		Reduction in root dry wt from nonsaline control	0	25	65
	0.15	2 hr/day (63 days)		25	28	78
	0.25	2 hr/day (63 days)		91	89	79

[a] Special soil moisture conditions are underlined; kPa = kilopascals; % turgid indicates amount of water in the plant leaf.

[b] A stimulation rather than a reduction.

Source: Modified from Table 11-9, U.S. Environmental Protection Agency (1978).

It appears that the stomata of plants grown under soil moisture stress close more rapidly in the presence of O_3 than stomata of plants under optimal water availability (Tingey et al., 1982; Olszyk and Tibbitts, 1981; U.S. Environmental Protection Agency, 1978). Such a plant response would reduce O_3 ingress and confer some resistance to O_3 injury.

Tingey et al. (1982) found that the leaf conductance of bean plants that were water-stressed decreased, compared with nonstressed plants, 24 hours after the stress was applied. A coincident reduction in plant response to O_3 (1 ppm for 1 hour) occurred. If plants were water-stressed for 7 days and then the water stress was relieved, leaf conductance and plant response to O_3 both increased.

A 2-yr field study was conducted to determine the effects of O_3 on the yield of normally irrigated and water-stressed cotton (Temple et al., 1985a). In the first year, which was hot and dry, ambient O_3 reduced the yield of cotton by 20 percent in the normally irrigated plots but did not affect the yield of the water-stressed plants. The second year was cooler, had less evapotranspiration, and had significantly less O_3 than the first. Under these conditions, cotton at both soil moisture treatments displayed the same response to O_3. The ambient O_3 reduced cotton yield by 15 percent.

Plants subject to long-term soil moisture stress may also exhibit morphological or functional changes, or both, that could modify the O_3 response. Drought or salt stress, which can confer long-term moisture stress, are more limiting to plant health than the air pollution stress that they may modify; hence, any of their protective effects are offset (U.S. Environmental Protection Agency, 1978).

It is important to recognize that plants grown under optimal soil moisture, as in irrigated fields or greenhouses, generally are particularly vulnerable to O_3 injury. On this basis, vegetation in natural ecosystems, for example, would be expected to be more sensitive to O_3 in years of normal rainfall than in years of drought.

6.3.2.2.5 Soil fertility. Nutrient balance is fundamental to plant growth; any imbalance could lead to variations in the O_3 response. Plant nutrients, including nitrogen, phosphorus, potassium, and sulfur, may all influence plant response to O_3 (U.S. Environmental Protection Agency, 1978). Results of studies cited in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) were inconsistent for a variety of reasons, including species differences and differences in experimental protocols and designs. Since then, additional data have appeared, but the relationship between soil fertility and O_3 sensitivity has not been clarified. Harkov and Brennan (1980) grew hybrid poplar seedlings with varied amounts of slow-release fertilizer, 18:16:12 (N:P:K), that yielded plants with foliar contents of 1.53, 2.69, 3.12, or 3.47 percent nitrogen. Visible injury was greatest in leaves containing 2.69 percent nitrogen when plants were exposed to an O_3 concentration of 0.10 ppm for 6 hours. Using an N:P:K ratio of 6:25:15, Heagle (1979a) found that potted soybean plants exposed to an O_3 concentration of 0.60 ppm for 1.5 hours were more sensitive when fertilized with 100 ml of solution at a rate of 0 or 7.5 g fertilizer/3.8 liters of water than when 15 or 22.5 g/3.8 liter of water was used. Optimum soybean growth was observed at fertilizer rates of 15.0 and 22.5 g/3.8 liters of water. Noland and Kozlowski (1979) reported that silver maple became more sensitive to O_3 (0.30 ppm for 6 hr for 2 successive days) when grown with 117 ppm potassium as compared to 0 to 2 ppm potassium for 6.5 wk. The authors suggested that potassium may stimulate the guard cells to open, thereby increasing the uptake of O_3 by this species. Dunning et al. (1974) found that pinto bean and soybean foliage were injured more severely by O_3 when plants were grown with low potassium levels (105 meq/liter) rather than normal levels (710 meq/liter). Greenhouse studies of tobacco showed a negative correlation between the calcium content of the leaf tissue and O_3-induced (0.25 ppm for 4 hr) foliar injury (Trevathan and Moore, 1976). This result was observed at eight combinations of O_3 concentration and exposure duration. Additional explanations for the variable response of plants to O_3 when grown with different fertility regimes have not been formulated.

6.3.2.3 Chemical Factors.

The chemical environment of plants (e.g., air pollutants, herbicides, fungicides, insecticides, nematocides, antioxidants, and chemical protectants) influences plant responses to O_3. These factors may be grouped into the subject areas of pollutant interactions and chemical sprays.

6.3.2.3.1 Pollutant interactions.

Components of ambient atmospheres such as SO_2, NO_2, and other pollutants may change, modify, or alter plant sensitivity to O_3. These substances all contribute to intensifying or reducing the effects of O_3 on the quality, quantity, or intended use of the plant and must be considered along with the discussion of biological (Section 6.3.2.1) and physical (Section 6.3.2.2) factors that modify plant responses to O_3. The magnitude of these modifications depends on the plant species, cultivar, pollutant concentration, duration and frequency of exposure, and the environmental and edaphic conditions in which plants are grown.

The study of the effects of pollutant combinations on plants is based on the premise that pollutants co-occur in the atmosphere, and that together they may induce more plant damage than that induced by the individual pollutants. Researchers have tried to develop terminology that is meaningful in evaluating the effects of pollutant mixtures on plants (Reinert, 1975; Ormrod, 1982; Ormrod et al., 1984). Two categories of plant response are possible when the effects of two pollutants (A and B) are evaluated. When one pollutant has no effect on plant response but the second one does, it is termed "no joint action." Thus, the term "joint action" implies that both pollutants have some effect on plant response. The concept of joint action can be further divided into subcategories that can be used to describe the response of plants to pollutants, A and B:

1. Additive response: $\text{Effect}_{AB} = \text{Effect A} + \text{Effect B}$
2. Interactive response: $\text{Effect}_{AB} \neq \text{Effect}_A + \text{Effect}_B$

The interactive response may be divided further into two types:

1. Synergism: $\text{Effect}_{AB} > \text{Effect}_A + \text{Effect}_B$
2. Antagonism: $\text{Effect}_{AB} < \text{Effect}_A + \text{Effect}_B$

Some studies use the term "greater (more) than additive" to mean synergism and the term "less than additive" to mean antagonism.

It is the purpose of this section to discuss the effects of the joint action of SO_2 plus O_3, NO_2 plus O_3, and NO_2 plus SO_2 plus O_3; and to identify the concentrations of O_3, alone or in combination with other pollutants, that cause yield loss.

6.3.2.3.1.1 Ozone and sulfur dioxide. The joint action of O_3 and SO_2 has been extensively studied. The previous criteria document (U.S. Environmental Protection Agency, 1978) stated that mixtures of O_3 plus SO_2 were of special interest because of the Menser and Heggestad (1966) study. In that study, a sensitive 'Bel W_3' cigar-wrapper tobacco exposed to mixtures of O_3 (0.03 ppm) and SO_2 (0.25 ppm) for 2 or 4 hr sustained 23 percent and 48 percent foliar injury, respectively; but no visible injury was produced by the same concentrations of the individual pollutants. The additive and frequently synergistic foliar-injury response of tobacco has been reported to occur in numerous tobacco cultivars and types. Menser and Hodges (1970), Grosso et al. (1971), and Hodges et al. (1971) determined the response of several Nicotiana species and various N. tabacum cultivars to SO_2 and O_3 mixtures. They found that O_3 and SO_2 acted synergistically and produced O_3-type symptoms on all cultivars of burley and Havana tobacco. When plants were fumigated for 4 hr with 0.03 ppm O_3 alone or with 0.45 ppm SO_2 alone, no injury was observed. When the gases were combined and the plants were exposed for the same length of time, foliar injury ranging from 5 percent to 15 percent was produced. Tingey et al. (1973b) exposed 11 species of plants to different combinations of O_3 and SO_2: either 0.05 or 0.1 ppm O_3 and 0.1, 0.25, or 0.5 ppm SO_2 for 4 hr. They observed additive and synergistic foliar-injury responses on five of the six species in Table 6-5 but not at all exposure combinations.

TABLE 6-5. SUMMARY OF EFFECTS OF SULFUR DIOXIDE AND OZONE MIXTURES ON FOLIAR INJURY

	Response at stated ppm SO_2/O_3 concentrations[a]			
Plant species	0.50/0.05	0.50/0.10	0.10/0.10	0.25/0.10
Alfalfa	-	+	+	+
Broccoli	+	0	+	0
Cabbage	0	+	0	0
Radish	0	+	+	+
Tomato	0	0	-	0
Tobacco, Bel W_3	+	+	0	+

[a] + = greater than additive; 0 = additive; - = less than additive.

Source: Tingey et al. (1973b).

Foliar injury symptoms decrease the aesthetic value of various types of woody ornamental and floricultural crop species (Section 6.4.3). Also, when foliage is the marketable plant part, substantial losses in quality and marketability of the crop result from the injury produced by the joint action of pollutants. The amount of foliar injury affects the amount of photosynthate produced by the plant. Thus, in many instances, foliar injury provides some indication of the potential for loss in weight, size, and number (yield) of the marketable plant part. Foliar-injury response from the joint action of pollutants needs continued study.

Since 1978, researchers have continued to use foliar injury as an indicator of the sensitivity of plant species and cultivars within a species to the joint action of O_3 and SO_2. Studies have included apple (Shertz et al., 1980a), grape (Shertz et al. 1980b), radish, cucumber, and soybean (Beckerson and Hofstra, 1979), begonia (Reinert and Nelson, 1980), and pea (Olszyk and Tibbitts, 1981). These results are summarized in Table 6-6. Although relatively high O_3 and SO_2 concentrations were used for only a few hours, most species displayed a synergistic injury response from the joint effects of the pollutants, supporting previous observations.

The chronic effects of the joint action of O_3 and SO_2 on the growth of radish, alfalfa, soybean, and tobacco (Table 6-7) were summarized in 1978 (U.S. Environmental Protection Agency, 1978). These four species represent a diverse group of plant species in terms of growth habit. Primary focus in earlier studies was on weight changes during the vegetative stage of growth, with the exception of one study (Heagle et al., 1974); however, radish root (hypocotyl), tobacco leaf weight, and alfalfa foliage (top) weight are the marketable portions of the plant. With the exception of alfalfa, the growth of each plant species was reduced in an additive manner by the joint action of the two pollutants. Soybean root (fresh weight) responded synergistically to the joint action of O_3 and SO_2 in one study (Tingey et al., 1973c).

The above data were obtained in greenhouse studies (except for Heagle et al., 1974). These data provided preliminary evidence that the joint action of O_3 and SO_2 at concentrations of 0.05 ppm and greater caused an additive reduction in plant yield. Additional studies of the joint action of O_3 and SO_2 on plant yield have been conducted since 1978 (Tables 6-8 and 6-9). More emphasis has been given to the influence of pollutant combinations on yield (weight, size, and numbers) as a measure of plant response, including the yield of flower, fruit, and seed portions of the plant (Table 6-8). Shew et al. (1982) exposed tomato to 0.2 ppm O_3 and SO_2 alone and together, two times per week, 2 hr each time for 8 wk. They demonstrated that the joint action of O_3 and SO_2 was synergistic, decreasing the weight of the largest fruit in each tomato cluster; but that the synergistic effects did not influence total fruit weight per plant.

Reinert and Nelson (1980) exposed five cultivars of begonia to 0.25 ppm O_3 and SO_2 alone and in combination for a total of 16 hr (4 hr/wk) over a 4-wk period. The joint action of O_3 plus SO_2 was antagonistic (cv. Schwabenland Red) and additive (cv. Fantasy), respectively, in producing a loss in flower

TABLE 6-6. FOLIAR INJURY RESPONSE OF VARIOUS PLANT SPECIES TO OZONE AND OZONE PLUS SULFUR DIOXIDE[a]

Species	Concentration[b], ppm		Exposure duration	Response	Foliar injury, %			Interaction[c] effect	Monitoring method[a]	Calibration method	Fumigation facility	Reference
	O_3	SO_2			O_3	SO_2	$SO_2 + O_3$					
Apple (Vance Delicious)	0.40	0.40	O_3-4 hr/day, 1 time SO_2-4 hr/day, 1 time	Foliar injury	24	8	26	-6	O_3-Mast meter SO_2-Not given	KI Permeation tubes	Controlled environment chambers	Shertz et al. (1980a)
(Imperial McIntosh)					30	9	22	-17				
(Golden Delicious)					27	19	19	-27				
Grape (Ives)	0.40	0.40	O_3-4 hr/day, 1 time SO_2-4 hr/day	Foliar injury	27	18	47	2	O_3-Mast meter SO_2-Not given	KI Permeation tubes	Controlled environment chambers	Shertz et al. (1980b)
(Delaware)					1	1	4	2				
Radish	0.15	0.15	O_3-6 hr/day, 5 days SO_2-4 hr/day, 5 days	Foliar injury	13	1	30	16	O_3 -UV Dasibi SO_2-Conductivity	Not given Not given	Exposure chambers in environmentally controlled room	Beckerson and Hofstra (1979)
Cucumber					27	9	54	18				
Soybean					18	0	0	-18				
Begonia (Schwabenland Red)	0.25	0.50	O_3-4 hr/day every 6 days, 4 times SO_2-4 hr/day every 6 days	Foliar injury	54	2	67	11	O_3-Chemiluminescence SO_2-Flame photometry	Monitor Labs Calibrator	CSIR in greenhouse	Reinert and Nelson (1980)
(Wisper 'O' Pink)					25	1	58	32				
(Fantasy)					2	0	13	11				
(Renaissance)					15	0	18	3				
(Turo)					8	0	12	4				
Pea	0.13	0.40	O_3-4 hr, 1 time SO_2-4 hr, 1 time	Foliar	0	0	32	32	O_3-Chemiluminescence SO_2-Thermo-electron (SO_2)	KI Gas-phase titration	Plexiglas chamber	Olszyk and Tibbits (1981)

[a] Where column entry is blank, information is the same as above.

[b] Concentrations of each gas were the same when given together as when given singly.

[c] The "interaction effect" is the effect from the combination of O_3 and SO_2 minus the individual effects of O_3 and SO_2 (see Section 6.3.2.3.1).

TABLE 6-7. GROWTH RESPONSE OF VARIOUS PLANT SPECIES TO OZONE AND OZONE PLUS SULFUR DIOXIDE

Species	Concentration[a], ppm		Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted)			Interaction[b] effect	Monitoring method	Calibration method	Fumigation facility	Reference
	O_3	SO_2			O_3	SO_2	$SO_2 + O_3$					
Radish (Cherry Belle)	0.05	0.05	8 hr/day, 5 days/wk, 5 wks	Top dry wt	10	0	10	0	O_3-Mast meter	KI	Chambers in green-house	Tingey et al. (1971a)
				Root dry wt	50	17	55	-12	SO_2-Conductivity	Colorimetric		
Alfalfa (Vernal)	0.05	0.05	8 hr/day, 5 days/wk 12 wk	Top dry wt	12	26	18	-20	O_3-Mast meter	KI	Chambers in green-house	Tingey and Reinert (1975)
				Root dry wt	22	29	24	-27	SO_2-Conductivity	Colorimetric		
Soybean (Dare)	0.05	0.05	7 hr/day, 5 days/wk 3 wk	Top fresh wt	2	+5	12	15	O_3-Mast meter	KI	Chambers in green-house	Tingey et al. (1973c)
				Root fresh wt	3	0	24	21	SO_2-Conductivity	Colorimetric		
Soybean (Dare)	0.10	0.10	7 hr/day, 5 days/wk, until harvest	Top fresh wt	65	+3	52	-10	O_3-Mast meter	KI	Field chambers	Heagle et al. (1974)
				Seed wt	54	4	63	5	SO_2-Flame photometry	Not given		
Tobacco (Bel-W_3)	0.05	0.05	7 hr/day, 5 days/wk, 4 wk	Leaf dry wt	1	14	30	15	O_3-Mast meter SO_2-Conductivity	KI Colorimetric	Chambers in green-house	Tingey and Reinert (1975)

[a] Concentrations of each gas were the same when given together as when given singly.

[b] The "interaction effect" is the effect from the combination of O_3 and SO_2 minus the individual effects of O_3 and SO_2 (see Section 6.3.2.3.1).

TABLE 6-8. YIELD RESPONSES OF VARIOUS PLANT SPECIES TO OZONE AND OZONE PLUS SULFUR DIOXIDE

Species	Concentration[a] ppm		Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted)			Inter-action effect[b]	Monitoring method	Calibration method	Fumigation facility	Reference
	O_3	SO_2			O_3	SO_2	$SO_2 + O_3$					
Tomato (Walter)	0.20	0.20	O_3-4 hr/day, 2 day/wk, 8 wk SO_2-4 hr/day, 2 day/wk, 8 wk	Largest fruit each cluster	1	2	18	15	O_3-Chemiluminescence SO_2-Flame photometry	Known source Permeation tube	Chambers in greenhouse (CSTR)[b]	Shew et al. (1982)
				Total fruit	5	4	4	-5				
Begonia (Schwabenland Red)	0.25	0.50	O_3-4 hr/day, every 6 days for 4 times, SO_2-4 hr/day every 6 days 4 for times	Flower wt	39	22	38	-23	O_3-Chemiluminescence SO_2-Flame photometry	Known source Permeation tube	Chambers in greenhouse (CSTR)	Reinert and Nelson (1980)
(Wisper 'O' Pink)	0.25	0.50		Flower wt	22	+16	28	22				
(Fantasy)	0.25	0.50		Flower wt	6	9	21	6				
(Renaissance)	0.25	0.50		Flower wt	55	43	54	-44				
(Turo)	0.25	0.50		Flower wt	+10	+11	4	25				
Snap bean (BBL 290) (BBL 274) (Astro)	0.065[b]	0.30	O_3-11 hr/day avg, 3 mo SO_2-6 hr/day, 5 day/wk, 5 wk	Green pod wt	2	16	44	26	O_3-Not given SO_2-Pulse fluorescence	Not given Permeation tube	Field chamber (open top)	Heggestad and Bennett (1981)
Tall fescue (Alta)	0.10	0.10	O_3 and SO_2 6 hr/day, once a week for 12 weeks	No. of tillers	+1	6	4	-1	O_3-UV SO_2-Pulse fluorescence	UV photometry greenhouse Permeation tube	Chambers in (1982a) (CSTR)	Flagler and Youngner (1982a)
	0.20	0.10			6	6	+12	0				
	0.30	0.10			+5	6	19	18				
	0.10	0.10		Top dry wt	+3	5	18	16				
	0.20	0.10			19	5	19	-5				
	0.30	0.10			18	5	53	30				
Alfalfa (Mesa-Sirsa)	0.05	0.05	O_3-6 hr/day, SO_2-24 hr/day, 68 days	Foliage dry 68 days	49		46	-3	O_3 Mast meter	KI	Field chamber (closed top	Neely et al. (1977)

[a] Concentrations of each gas were the same when given together as when given singly.

[b] CSTR = Continuous stirred tank reactor exposure chamber.

[c] The "interaction effect" is the effect from the combination of O_3 and SO_2 minus the individual effects of O_3 and SO_2 (see Section 6.3.2.3.1).

TABLE 6-9. INFLUENCE OF MIXTURES OF OZONE AND SULFUR DIOXIDE ON SOYBEAN YIELD[a]

Seasonal 7 hr/day O_3 concn., ppm	Yield, % reduction from control			
	Seasonal 4 hr/day SO_2 concn., ppm			
	0.00	0.026	0.085	0.367
0.00	0 (412)[a]	+6.3	+3.4	30.6
0.055	7.5	22.8	20.1	42.5
0.068	22.8	24.0	28.6	53.3
0.085	33.7	42.2	43.4	54.1
0.106	40.3	39.3	51.9	62.6

[a] Mean yield (grams of seed) from eight 1-meter-row samples.

Source: Heagle et al., 1983c.

weight. The mean yield (flower weight) from the joint effects of O_3 and SO_2 ranged from 1 percent (Schwabenland Red) to 15 percent (Fantasy) greater than the loss resulting from O_3 alone.

The joint action of O_3 and SO_2 on the growth and yield components of tall fescue was studied by Flagler and Youngner (1982a). Fescue was exposed to O_3 concentrations of 0.0, 0.1, 0.2, and 0.3 ppm and 0.0 and 0.1 ppm SO_2 for 6 hr/day, once a wk for 12 wk. The joint action of SO_2 in the presence of increasing concentrations of O_3 caused additive decreases in fescue total dry weight, root dry weight, and the root-to-shoot ratio. For example, O_3 decreased total dry weight 49 percent at 0.3 ppm O_3; but in the presence of 0.1 ppm SO_2 there was an additional 11 percent loss in total dry weight. Ozone and SO_2 acted synergistically to decrease the number of tillers in fescue but the synergism depended on the O_3 concentration. These studies were done in a charcoal-filtered-air greenhouse in CSTR exposure chambers.

Recently, studies of the combined action of O_3 and SO_2 have been conducted in open-top field chambers (Heagle et al., 1983c; Heggestad and Bennett, 1981) and large CSTR field chambers (Foster et al., 1983b; and Oshima, 1978). In these experiments, O_3 levels near ambient, as well as increasing O_3 concentrations above ambient, were used in combination with two or more concentrations of SO_2. Heagle et al. (1983c) exposed soybean to various concentrations of O_3 for 7 hr daily and 4 concentrations of SO_2 for 4 hr/day. Both gases were added for 111 days (Table 6-9). The high concentration of SO_2 decreased the amount of visible injury from increasing concentrations of O_3. The joint action of O_3 and SO_2 on soybean seed weight per meter of row at lower concentrations appeared to be additive, but as the concentrations of both pollutants increased there was an antagonistic O_3-plus-SO_2 interaction. The nature of the joint action was similar to that for visible injury: as SO_2 increased to 0.367 ppm, the loss of seed weight from increasing O_3 concentrations was less than at lower concentrations of SO_2. For example, at 0.367 ppm SO_2 and 0.085 ppm O_3 there was a 54.1 percent seed-weight loss compared to that at 0.367 ppm SO_2 alone. At 0.026 ppm SO_2 and 0.085 ppm O_3 there was a 42.2 percent seed-weight loss, compared to that at 0.026 ppm SO_2 alone (Table 6-8). The two highest mean SO_2 concentrations were higher than usually occur in the United States and even the concentration of 0.026 ppm SO_2 is higher than that found in the ambient air at most locations (U.S. Environmental Protection Agency, 1983).

Using a field fumigation (tubular release) system, Reich and Amundson (1984) exposed soybean to O_3 and/or SO_2 in a 3 x 3 factorial design. The plants were exposed to levels of O_3 and SO_2 above ambient for about 5 hr/day for 16 days from mid-August to mid-September. There was no significant interaction between O_3 and SO_2 on soybean yield.

Heggestad and Bennett (1981) exposed three cultivars of bean to increasing concentrations of SO_2 (0.06, 0.12, 0.3 ppm) for 6 hr/day in charcoal-filtered and unfiltered ambient air, using open-top field chambers. The beans were exposed daily 5 days/wk for 31 days. During the study period (July-August), the average daily maximum O_3 concentration during the SO_2 fumigation period (9:00 a.m. to 3:00 p.m.) was 0.065 ± 0.025 ppm. Sulfur dioxide (0.30 ppm) reduced snap bean yields (all cultivars) in nonfiltered air (O_3) by 44 percent compared to a 16 percent reduction in charcoal-filtered air. At 0.06 ppm SO_2, the yield of cv. 'Astro' was reduced more in nonfiltered than in filtered air. The SO_2 concentrations used in this study, however, were higher than typically occur in the United States (U.S. Environmental Protection Agency, 1983).

In southern California, Oshima (1978) and Foster et al. (1983b) conducted studies to determine the joint action of SO_2 and photochemical oxidants. A range of photochemical oxidant concentrations was obtained by combining various proportions of charcoal-filtered air and ambient air containing oxidants to yield various concentrations of oxidants which were added to the CSTR-type field exposure chambers. Sulfur dioxide (0.0 or 0.1 ppm) was added to the chambers for 6-hr intervals approximately 47 times over a 76-day period for beans (Oshima, 1978) and 4 to 5 days/wk over a 10-wk period for potato (Foster et al., 1983b). In the bean study (Oshima, 1978), the ozone concentration exceeded 0.20 ppm frequently; the total ozone dose ranged from approximately 10.9 ppm-hr in the charcoal-filtered air chambers to approximately 83 ppm-hr in the chambers receiving ambient ozone. In the potato study (Foster et al., 1983b), the maximum hourly concentration was 0.27 ppm; for the remainder of the study, the concentration never exceeded 0.20 ppm. The total ozone dose ranged from 4.9 ppm-hr in the charcoal-filtered air chambers, to approximately 44 ppm-hr in the chambers receiving ambient ozone. The kidney bean yield was less in the presence of ambient oxidant plus SO_2 except at the high oxidant concentrations, when the yields were more nearly similar. Similar studies with potato exposed to SO_2 and partially filtered ambient air containing O_3 resulted in no evidence of joint action on tuber yield (Foster et al., 1983b).

In summary, recent studies on the effects of O_3 and SO_2 on the yield of various plant species have found the effects of O_3 and SO_2 to be additive (equal to the combined effects of the individual pollutants) for begonia flower weight, fescue top and root dry weights, soybean seed weight, and snap bean and green bean yield. Synergistic interaction was identified for the effects of O_3 and SO_2 on the largest tomato fruit in each cluster, the number of fescue tillers, and kidney bean yield. Examples of antagonistic joint action occurred in one cultivar of begonia and in soybean seed weight at the highest SO_2 concentrations. These effects varied with the concentration of pollutants, the plant response measured, species, and cultivar. Thus, observations were significant enough to propose the following general concepts:

1. When concentrations of O_3 and SO_2 are below or at the threshold for visible injury, synergistic interaction may occur.
2. As concentrations of O_3 and SO_2 increase in mixture above the injury threshold, yield loss from joint action may be additive.
3. When both pollutants are present in high concentrations, the joint action of O_3 and SO_2 may be antagonistic, such that further weight loss is mimimal.
4. In field studies, the addition of SO_2 generally did not influence the O_3 response unless the concentrations and exposure frequencies were much greater than the SO_2 concentrations and frequencies of occurrence that are typically found in the ambient air in the United States.

Relative to the last item above, an analysis of ambient air monitoring data at various locations determined the frequency of the co-occurrence of pollutant pairs (O_3/SO_2, O_3/NO_2) during a 5-month summer season (May through September) (Lefohn and Tingey, 1984). Co-occurrence was defined as the simultaneous occurrence of hourly averaged concentrations of 0.05 ppm for both pollutants of the pair. Most of the monitoring sites analyzed by Lefohn and Tingey experienced 10 or fewer periods (hours) of co-occurrence during the 5-month summer season (May through September).

6.3.2.3.1.2 Ozone and nitrogen dioxide. Although the effects of NO_2 and O_3, alone and in mixture, have not generally been studied, recent reports comparing two- and three-pollutant mixture treatments include NO_2 plus O_3 combinations. Kress and Skelly (1982) have studied the responses of seven tree species to NO_2 (0.1 ppm) and O_3 (0.1 ppm) alone and in mixture for 6 hr/day, for 28 consecutive days (Table 6-10). Virginia and loblolly pine growth, as measured by plant height, was significantly suppressed by the O_3-plus-NO_2 treatment, but not by the individual pollutants. Nitrogen dioxide alone significantly suppressed root dry weight of sweetgum; however, the joint action of O_3 plus NO_2 was antagonistic on sweetgum root dry weight and white ash root dry weight.

6.3.2.3.1.3 Ozone plus nitrogen dioxide and sulfur dioxide. The previous criteria document (U.S. Environmental Protection Agency, 1978) makes no reference to the effects of mixtures using three pollutants. Since then, however, experiments have been designed to study the effect of increasing concentrations of NO_2, SO_2, and O_3 in mixture (Table 6-11). Reinert and Gray (1981) exposed radish plants one time for 3 or 6 hr to 0.2 or 0.4 ppm of NO_2, SO_2, or O_3, or combinations. They found no interaction for either two- or three-gas mixtures, even though the decrease in hypocotyl weight by O_3 was further reduced by NO_2 alone, SO_2 alone, or NO_2 plus SO_2, which suggests an additive response. Reinert and Sanders (1982) and Sanders and Reinert (1982b) reported similar results in radish following repeated exposures at different ages.

Marigold was exposed at different ages for 3 hr to 0.3 ppm of each pollutant, three times/wk for 1 wk (Sanders and Reinert, 1982b). Ozone alone decreased flower dry weight but the interaction of NO_2 or O_3 with SO_2 was apparently antagonistic. Similar results were reported for marigold exposed repeatedly 3 days a week for 3 wk. Reinert and Heck (1982) exposed snap beans

TABLE 6-10. YIELD RESPONSES OF SELECTED TREE SPECIES TO OZONE PLUS NITROGEN DIOXIDE[a]

Species	Concentration[b], ppm		Exposure duration	Response	Height and top dry wt, % reduction from control (negative unless otherwise noted)			Interaction effects[d]
	O_3	NO_2			O_3	NO_2	$O_3 + NO_2$	
Loblolly pine	0.10	0.10	6 hr/day, 28 days	Height growth	17	15	39	7
				Top dry wt	21	22	26	-17
				Root dry wt	13	17	26	-4
Loblolly pine (6-13 x 2-8)[c]	0.10	0.10	6 hr/day, 28 days	Height growth	25	11	24	-24
				Top dry wt	11	10	4	-17
				Root dry wt	31	14	17	-28
Pitch pine	0.10	0.10	6 hr/day, 28 days	Height growth	14	16	26	-4
				Top dry wt	+14	20	11	5
				Root dry wt	0	11	15	4
Virginia pine	0.10	0.10	6 hr/day, 28 days	Height growth	11	13	23	-1
				Top dry wt	2	1	1	-2
				Root dry wt	19	7	19	-19
Sweetgum	0.10	0.10	6 hr/day, 28 days	Height growth	27	32	28	-31
				Top dry wt	30	25	21	-34
				Root dry wt	45	27	48	-24
White ash	0.10	0.10	6 hr/day, 28 days	Height growth	20	+5	16	1
				Top dry wt	37	1	37	-1
				Root dry wt	55	37	52	-40
Green ash	0.10	0.10	6 hr/day, 28 days	Height growth	19	+1	22	4
				Top dry wt	17	10	29	2
				Root dry wt	12	18	19	-11
Willow oak	0.10	0.10	6 hr/day, 28 days	Height growth	+5	10	14	9
				Top dry wt	+1	24	13	-10
				Root dry wt	+11	14	12	9

[a] Plants were exposed in continuously stirred tank reactor (CSTR) exposure chambers in a greenhouse. Ozone and NO_2 were monitored using chemiluminescent analyzers which were calibrated with known sources of each pollutant.

[b] Concentrations of the combination were the same as the single gases.

[c] Indicates seeds were from a full-sibling collection.

[d] The "interaction effect" is the effect from the combination of O_3 and NO_2 minus the individual effects of O_3 and NO_2 (see Section 6.3.2.3.1).

Source: Kress and Skelly, 1982.

TABLE 6-11. YIELD CHANGE IN VARIOUS PLANT SPECIES EXPOSED TO OZONE, SULFUR DIOXIDE, AND NITROGEN DIOXIDE

Species	Concentration[a], ppm			Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted)							Monitoring method	Calibration method	Fumigation facility[b]	Reference
	O_3	SO_2	NO_2			O_3	SO_2	NO_2	SO_2+NO_2	O_3+SO_2	O_3+NO_2	O_3+SO_2+NO_2				
Snap Bean	0.15	0.15	0.15	4 hr, 3 times/wk 4 wks	Green bean fresh wt	27	9	+12	20	6	25	27	O_3, NO_2-chemiluminescence; SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Reinert and Heck (1982)[c]
Marigold	0.30	0.30	0.30	3 hr/day, 3 days/wk, 3 wks	Flower wt	20	47	+16	13	23	+4	20	O_3, NO_2-chemiluminescence; SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Reinert and Sanders (1982)
Marigold	0.30	0.30	0.30	3 hr/day, 3 days/wk, 1 wk	Flower wt	41	49	23	47	25	39	20	O_3, NO_2-chemiluminescence SO_2 Flame photometry	Known source	Chambers in greenhouse (CSTR)	Sanders and Reinert (1982b)
Radish	0.30	0.30	0.30	3 hr/day, 3 days/wk, 1 wk	Hypocotyl	30	+21	+10	+16	43	33	65	O_3, NO_2-chemiluminescence SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Sanders and Reinert (1982b)
Radish	0.40	0.40	0.40	3 hr + 6 hr 1 time	Hypocotyl	20	4	0	13	24	23	36	O_3, NO_2-chemiluminescence SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Reinert and Gray (1981)
Azalea	0.25	0.25	0.25	3 hr/day, 6 times in a 4-wk period	Foliage	6	7	0	17	22	16	27	O_3, NO_2-chemiluminescence; SO_2-flame photometry	Known source	Chambers in greenhouse (CSTR)	Sanders and Reinert (1982a)

TABLE 6-11 (cont'd). YIELD CHANGE IN VARIOUS PLANT SPECIES EXPOSED TO OZONE, SULFUR DIOXIDE, AND NITROGEN DIOXIDE

Species	Concentration[a], ppm			Exposure duration	Response	Yield, % reduction from control (negative unless otherwise noted)							Monitoring method	Calibration method	Fumigation facility[b]	Reference
	O_3	SO_2	NO_2			O_3	SO_2	NO_2	SO_2+NO_2	O_3+SO_2	O_3+NO_2	$O_3+SO_2+NO_2$				
Kentucky bluegrass (12 cultivars)	0.15	0.15	0.15	O_3-hr/day, 10 days SO_2-cont. 10 days NO_2-, continuous, 10 days	Leaf area	5	12	6	NT[d]	NT	NT	16	O_3, UV Dasibi fluorescence NO_2, chemiluminescence	Not given SO_2, phase chamber	Plexiglas exposure	Elkiey and Ormrod (1980)
Red top grass	0.15	0.15	0.15	SAA	Leaf area	14	12	12	NT	NT	NT	28				
Creeping bentgrass	0.15	0.15	0.15	SAA[e]	Leaf area	7	18	8	NT	NT	NT	26				
Colonial bentgrass	0.15	0.15	0.15	SAA	Leaf area	15	6	13	NT	NT	NT	27				
Red fescue (2 cultivars)	0.15	0.15	0.15	SAA	Leaf area	16	0	0	NT	NT	NT	22				
Perennial ryegrass	0.15	0.15	0.15	SAA	Leaf area	20	+7	2	NT	NT	NT	13				

[a] Concentrations of the combinations were the same as two single gases, except for bean exposed at 0.05 (O), 0.1 or 0.15 (SO) and 0.05 or 0.1 (NO_2).

[b] CSTR = Continuous stirred tank reactor exposure chamber.

[c] Derived from experimental data.

[d] NT = Exposure combination not tested.

[e] SAA = Exposure condition same as above.

27 times intermittently for 3 hours each time over 6.5 wk to increasing concentrations of SO_2 (0.0, 0.1, 0.15 ppm) and NO_2 (0.0, 0.05, 0.1 ppm) in the presence of 0.05 ppm O_3. Ozone alone decreased bean pod weight 10 percent, while NO_2 (0.1 ppm), SO_2 (0.15 ppm), and O_3 (0.05 ppm) together decreased pod weight by 31 percent. Reinert and Heck (1982) exposed 16-day-old radish plants one time for 3 hr to three concentrations (0.0, 0.2, and 0.4 ppm) or (0.1, 0.2, and 0.4 ppm) of NO_2, SO_2, and O_3 at all 27 (3 x 3 x 3) treatment combinations (Table 6-12). In both experiments, the reduction in size of radish hypocotyls was predominantly additive and linear within the range of concentrations used. The above studies were conducted primarily under greenhouse conditions but some of the species studied, such as marigold, tomato, and azalea, are grown commercially in greenhouses. The concentrations of SO_2 and NO_2 ($\leqq$ 0.4 ppm) are below the concentration of each pollutant individually (SO_2, 0.5 ppm, and NO_2, 1 to 2 ppm) that causes visible injury for a single exposure (Tingey et al., 1971b).

Several turf grass species and cultivars were exposed to O_3, SO_2, and NO_2 individually, and to the three pollutants combined to determine the effects on leaf area (Elkiey and Ormrod, 1980). The three-pollutant combination reduced the leaf area of only 4 of the 12 Kentucky bluegrass cultivars. The three-pollutant combination had no significant effect on red top, creeping bentgrass, and colonial bentgrass, but it did significantly reduce the leaf area of perennial ryegrass and one of the two red fescue cultivars.

The results from the pollutant interaction studies cited in this section demonstrated that the joint action of O_3 with SO_2 or NO_2 or both decreased the yield of several crop species more than O_3 alone. Sulfur dioxide usually modified the response to O_3 in an additive way. Yield losses resulting from O_3 exposure were further decreased by SO_2 in radish (5 percent), alfalfa (6 percent), soybean seed weight (9 percent), and tobacco (7 percent). These effects were at concentrations of O_3 and SO_2 $\leq$ 0.05 ppm and greater. At higher concentrations of O_3 and SO_2 (0.2 to 0.5 ppm), yield losses from O_3 exposure were further reduced by SO_2 in begonia flower weight 6 to 15 percent depending on the cultivar; in kidney bean 11 to 28 percent, depending on the O_3 concentration; in potato, 11 to 16 percent; in soybean seed weight, 11 to 12 percent; and in fescue, $\leq$ 24 percent. Additional information concerning pollutant dose and frequency of exposure at which these effects take place is needed.

TABLE 6-12. EFFECTS OF NITROGEN DIOXIDE IN COMBINATION WITH SULFUR DIOXIDE OR OZONE, OR BOTH, ON RADISH ROOT FRESH WEIGHT AT THREE CONCENTRATIONS OF EACH GAS[a]

(grams)

SO_2, ppm	O_3, ppm	NO_2, ppm		
Experiment 1		0.1	0.2	0.4
0.1	0.1	9.5	8.8	8.4
	0.2	7.3	7.7	4.6
	0.4	4.6	3.0	2.9
0.2	0.1	9.5	9.5	6.2
	0.2	6.3	5.3	5.1
	0.4	2.9	3.3	2.7
0.4	0.1	8.3	6.6	4.9
	0.2	5.6	5.0	3.9
	0.4	2.3	3.0	3.0
Experiment 2		0.0	0.2	0.4
0	0	15.2	16.9	14.4
	0.2	12.4	11.0	9.6
	0.4	6.6	5.3	8.0
0.2	0	16.7	17.2	11.9
	0.2	11.2	7.3	7.6
	0.4	6.8	5.3	4.8
0.4	0	17.2	13.2	11.4
	0.2	9.5	7.2	5.8
	0.4	5.1	5.6	4.3

[a] Means represent 20 (exp. 1) or 12 (exp. 2) plants. Plants were exposed once for 3 hr at 16 days from seed and were harvested at 23 days from seed.

Source: Reinert and Heck (1982).

The initial studies on the effects of mixtures of NO_2, SO_2, and O_3 have involved the co-occurrence of these pollutants. The sequential effects of pollutant mixtures need to be investigated. In addition, more monitoring data are needed for each of the three pollutants so that realistic occurrences and concentrations can be part of the experimental design for assessing plant response.

6.3.2.3.1.4 Ozone and other pollutants. The effects of O_3 in combination with heavy metals have been studied in several plant species. Zinc and cadmium reacted synergistically with O_3 (0.30 ppm for 6 hours) in producing visible injury and chlorophyll loss in garden cress and lettuce (Czuba and Ormrod, 1974). The combination of cadmium (Cd) and O_3 induced earlier development of necrosis and chlorosis and the injury was observed at lower O_3 plus Cd levels than for the individual treatments (Czuba and Ormrod, 1981). Cadmium and nickel (Ni) concentrations of 1, 10, and 100 µmol in the nutrient solution interacted to reduce root and shoot growth of peas (Ormrod, 1977). Ozone exposure increased the Cd and Ni effects but the increase was less than additive. Low concentrations of Cd and Ni, however, tended to enhance O_3 phytotoxicity. The interaction of Cd and O_3 was influenced by both concentration and the environmental conditions. Tomato plants grown at 0.25 and 0.75 mg Cd/ml developed only slight foliar injury when exposed to O_3 (0.20 ppm for 3 hours) under cloudy skies; whereas the Cd treatment alone had no significant effect (Harkov et al., 1979). In full sun there was extensive O_3 injury and the joint response was synergistic. In pea leaves, alterations in cellular ultrastructure increased following exposure to ozone (0.50 ppm) when plants were grown in nutrient solutions containing 100 µmol nickel sulfate (Mitchell et al., 1979).

Quaking aspens treated with 10 µg Cd/ml for 30 days displayed significantly more foliar injury when exposed to ambient air in New Jersey (during the 30 days of Cd treatment) or exposed to 0.20 ppm O_3 for 2.5 hours (Clarke and Brennan, 1980). When plants were exposed to 0.30 ppm O_3, the Cd enhancement of injury was not apparent.

The limited published data indicate that heavy metals can increase the phytotoxic reactions of ozone. At the present time, it is not possible to assess the risk from the joint action of gaseous and heavy metal pollutants to vegetation. In industrial areas, along heavily travelled highways, and on crop lands fertilized with sludge, however, there is the possibility for interactive effects.

6.3.2.3.2 Chemical Sprays. A variety of agricultural chemicals commonly used by growers to control diseases and insects and other pests on crops and research plantings can modify vegetational response to air pollutants (Reinert and Spurr, 1972; Sung and Moore, 1979). Certain fungicides, insecticides, nematocides, and herbicides have been found to change the sensitivity of plants to ozone.

Protection from or reduction of O_3 injury to vegetation is significant to growers of economically important crops in areas of high ozone concentrations. In addition, the control of O_3 injury to plants in the field can be of assistance to scientists attempting to determine how O_3 injures plants. The report by Kendrick et al. (1954) that fungicides used as sprays or dusts protected pinto bean foliage from oxidant-induced plant damage alerted the scientific community to the fact that agricultural chemicals could protect vegetation from O_3 injury. Since that time, it has been shown that other chemicals, including ascorbic acid sprays (Freebairn, 1963; Freebairn and Taylor, 1960), antiozonants (Rich and Taylor, 1960), anti-transpirants (Gale and Hagan; 1972, 1966), stomatal regulators (Rich, 1964), growth regulators (Cathey and Heggestad, 1973), and some herbicides can offer some protection against ozone injury.

A comprehensive review of plant protectant sprays and their uses is found in Ozone and Other Photochemical Oxidants (National Research Council, 1977). The degree of plant protection obtained from O_3 injury and the species tested are listed in Table 6-13.

Nematocides increase the sensitivity of vegetation to O_3, but nematicides in combination with certain fungicides decrease sensitivity to O_3. Miller et al. (1976) noted that pinto bean and tobacco growing in sand or soil treated with the contact nematocides, phenamiphos, fensulfothion, aldicarb, and oxafothion were more sensitive to ambient O_3. Adding benomyl or carboxin, both fungicides, to the soil containing the contact nematocides caused the plants to become highly resistant to O_3 injury. Benomyl or carboxin used alone also induced plant resistance to O_3 injury.

The influence of selected herbicides on the O_3 sensitivity of tobacco and other crop plants has been studied with differing results. Carney et al. (1973) demonstrated that pebulate increased O_3 injury to tobacco but that benefin decreased O_3 injury. The studies of Sung and Moore (1979), however, failed to confirm the observation that pebulate increased O_3 sensitivity. Sung and Moore suggested that the difference in results occurred either because

TABLE 6-13. PROTECTION OF PLANTS FROM OXIDANT INJURY BY APPLICATION OF PROTECTIVE CHEMICALS

Plant species	Pollutant protected from:	Chemical (Concentration)[a]	Type of protectant	Degree of protection, %[b]
Bean, cultivar Pinto	Oxidant	K-Ascorbate (0.01 M)	Antioxidant	52
Petunia	Oxidant	K-Ascorbate (0.01 M)	Antioxidant	39
Tobacco	Oxidant	Zn-ethylenebisdithiocarbamate dust (variable)	Fungicide	44
Tobacco, cultivar White Gold	Oxidant	Phygon XL (variable)	Antioxidant	89
Tobacco, cultivar White Gold	Oxidant	Phygon XL (variable)	Antioxidant	78
Tobacco, cultivar White Gold	Oxidant	4,4-Dioctyldiphenylamine in butyl latex	Antioxidant	100
Bean, cultivar Pinto	Oxidant	Zineb (normal use)	Fungicide	91
Bean, cultivar Pinto	Ozone	Zineb (normal use)	Fungicide	97
Azalea	Oxidant	Benomyl (60-ppm drench)	Fungicide	96
Bean, cultivar Pinto	Ozone	Carboxin (2.3 ppm in soil)	Fungicide	95
Radish	Ozone	N-6-Benzyladenine (30-ppm spray)	Growth substance	100
Poinsettia	Ozone	Ancymidol (100-ppm spray)	Growth retardant	100
Poinsettia	Ozone (chronic)	Benomyl (500-ppm drench)	Fungicide	57
Bean, cultivar Pinto	Ozone	Folicote (0.5% spray)	Wax emulsion	92
Bean, cultivar Pinto	Ozone	Benomyl (5 ppm in nutrient solution)	Fungicide	97
Bean and cucumber	Ozone	Benomyl (80 ppm in soil)	Fungicide	94
Grape	Ozone	Benomyl (6.7 kg/ha, 6 times)	Fungicide	53
Bean, cultivars Tempo and Pinto	Ozone	Benomyl (0.25 to 0.36%, 4 weekly sprays)	Fungicide	75
Bean, cultivars Tempo and Pinto	Oxidant	Carboxin (10% granular as soil amendment, 8 g/5-m row)	Fungicide	100
Tobacco	Ozone (0.50 ppm, 2 hr)	Piperonylbutoxide (2 mM solution)	Insecticide	99
Tobacco	Ozone (0.35 ppm, 2 hr)	Safroxane	Insecticide	76
Bean, cultivar Tempo	Oxidant	Benomyl (0.24% spray)	Fungicide	32 to 41[c]
Grass, annual blue	Ozone (0.25 ppm, 2 hr)	Benomyl (60-ppm amendment)	Fungicide	85
Bean, cultivar Pinto	Ozone (0.30 ppm, 4 hr)	Triarimol	Fungicide	81
Bean, cultivar Pinto	Ozone (0.25 ppm, 4 hr)	Benomyl (1.60-μg/g soil amendment)	Fungicide	98
Bean, cultivar White	Ozone (0.13 to 0.50 ppm, 0.5 hr)	Ascorbic acid	Antioxidant	75
Petunia	Oxidant	SADH (0.5% spray)	Growth retardant	82
Tobacco	Oxidant	Benomyl (25-ppm drench)	Fungicide	68
Tobacco	Oxidant	Benomyl (0.18% spray)	Fungicide	59
Tobacco	Ozone	Peroxidase (0.10 ppm injected)	Enzyme	89

[a] These are applied as sprays unless otherwise noted.

[b] Percent reduction in plant injury from ozone as a result of the protectant treatment.

[c] Increase in yield by protectant application.

Source: Modified from National Research Council (1977).

the plants used were of different ages or because the O_3 concentrations used in the respective experiments differed. Reilly and Moore (1982), however, stated that pebulate had no consistent effect upon tobacco sensitivity to O_3.

Benomyl, specifically, and fungicides in general were discussed extensively as plant protectants in the National Research Council report (1977) because they have been the most widely studied protectants. Benomyl (methyl-1-butylcarbamoyl-2-benzimidazolecarbamate) has been used as a foliar spray, soil drench, and a soil amendment (National Research Council, 1977) and was found to reduce O_3 injury in a wide range of plant species (Table 6-13). Benomyl, while usually offering protection against O_3 injury, does not prevent PAN injury (Pell, 1976; Pell and Gardner, 1975; Pell and Gardner, 1979).

Antioxidants, chemical compounds that prevent food spoilage and discoloration and prevent rubber from reacting with O_3, have also been found to reduce O_3 injury in vegetation (Kendrick et al., 1962). In agricultural practice, antioxidants are used as synergists with insecticides, herbicides, and fungicides to increase their effectiveness. For example, antioxidants increase the potency of a certain insecticide by decreasing the rate at which insects are able to detoxify it.

Piperonyl butoxide (α-[2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyltoluene), a synergist used with pyrethrum insecticides, is highly effective in protecting tobacco leaves from O_3 injury (Koiwai et al., 1974; Koiwai and Kisaki, 1976; Koiwai et al., 1977). Koiwai et al. (1977) determined that most compounds having a synergistic activity with pyrethrum insecticides are, in general, effective in preventing ozone injury to tobacco leaves. Rubin et al. (1980) tested the protective capability of piperonyl butoxide when applied to navy bean cultivars '0686' and '0670' and found that both cultivars were protected by piperonyl butoxide, but only if it was used as a spray, not as a soil treatment. Piperonyl butoxide was slightly phytotoxic, but the symptoms resulting from the spray were not similar to those characteristic of ozone injury. Santoflex 13, (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine), an antioxidant, is used to protect rubber from ozone attack. Gilbert et al. (1977) found that bean, muskmelon cultivar 'Delicious 51,' and tobacco cultivar 'Bel W-3' were protected by Santoflex dust against visible injury when they were exposed to concentrations of O_3 up to 0.35 ppm in chamber studies.

Ethylenediurea (EDU) [N-(2-(2-oxo-1-imidazolidinyl)ethyl)-N-phenylurea], an antioxidant, has been widely used to reduce O_3 injury to vegetation. Pinto beans sprayed to run-off with 500 μg/ml EDU usually survived exposure to O_3 at concentrations of 0.8 ppm for 150 min without visible injury (Carnahan et al., 1978). Untreated plants exposed under the same conditions developed ozone injury symptoms over the entire surface area of the primary leaves.

Hofstra et al. (1978) found EDU to be more effective than benomyl or carboxin in suppressing O_3 injury on the highly sensitive navy bean growing in the field. It reduced bronzing, delayed leaf drop, and increased the yield up to 36 percent in plants exposed to hourly mean concentrations of O_3 at 0.1 to 0.3 ppm.

Pinto bean plants grown in pots received the greatest protection from O_3 injury when treated with EDU 3 to 7 days before a 6-hr exposure to O_3 concentrations of 0.10 to 0.76 ppm (Weidensaul, 1980). Plants received the most effective protection by EDU when O_3 concentrations were 0.41 ppm or higher. Foliage that had not yet been formed at the time the chemical was applied was not protected. The most extensive testing of the protective capabilities of EDU has been done by Cathey and Heggestad (1982a,b,c), who studied the effects of EDU (as either a foliar spray or soil drench) on the O_3 sensitivity of petunia (5 cultivars), chrysanthemum, and 44 other herbaceous species. In all cases they found that treatment with EDU reduced the O_3 injury. In addition to herbaceous species, EDU also reduced O_3 injury in woody vegetation (McClenahan, 1979; Cathey and Heggestad, 1982c).

Farmers and others growing crops in areas where high O_3 concentrations exist should be aware, as studies cited above indicate, that agricultural chemicals commonly used to protect plants from a variety of fungi, insects, and nematodes can modify the response of the vegetation to O_3 exposure. Antioxidants used in insecticides and herbicides to increase their effectiveness can also change the way plants respond to O_3 exposure. In general, nematocides seem to increase O_3 sensitivity, while fungicides and antioxidants have a protective effect when sprayed or drenched onto crops. Studies with herbicides have shown no general trend. Because no two of the chemical compounds that have been studied appear to function in the same way, it is not possible to generalize. At the present time, the protectants do not appear to be cost-effective to the extent that they can be generally prescribed for protecting plants from O_3 injury, but they may provide protection from ozone injury in addition to their primary function.

6.4 OZONE EXPOSURE AND RESPONSE

Plant responses to O_3 may be manifested as biochemical, physiological, visible injury, growth, yield, reproduction, and ecosystem effects. Biochemical and physiological alterations are the fundamental cause of all other effects, and were briefly described in Section 6.3. Visible foliar symptoms are frequently the first indication of the effects of air pollution on vegetation, but they may be difficult to distinguish from other stress effects. Although functional leaves are required for plant growth and yield, the loss of leaf area is not always well correlated with yield reductions. This lack of correlation may occur, if, for example, the plant has more leaf area than required to maintain the yield, or if plant or environmental factors other than leaf area limit yield. This concept is supported by the observation that plant yield is not well correlated with leaf photosynthetic rate. The lack of correlation between visible injury and yield is most common when the plant foliage is not the usable or marketable portion of the plant (yield). In this section, yield loss refers to the impairment of the intended use of the plant as described in Section 6.2.5. Foliar injury on ornamental plants and leafy vegetables; effects on native species; reductions in fruit, grain, foliage, or root production by agricultural species; or adverse changes in plant quality and aesthetic value can be considered yield loss for specific crops. Furthermore, reproductive capacities may be altered as a result of these responses; and this alteration may lead to changes in populations and, eventually, ecosystem modification (see Chapter 7).

In the chapter on vegetational effects in the previous criteria document (U.S. Environmental Protection Agency, 1978), emphasis was placed mainly on visible injury and growth effects. Most of the growth effects discussed concerned plant parts other than those of primary importance for yield. This emphasis was dictated by the kind of data available at that time. The summary figures and tables in the previous criteria document (U.S. Environmental Protection Agency, 1978) emphasized foliar injury responses (see Figures 6-3, 6-4, and 6-5 and Table 6-14). The visible injury data were summarized by presenting limiting values (Figures 6-3 and 6-4); i.e., those concentrations below which visible injury was unlikely and presumably at which reduced growth and yield would not occur. Another approach was to determine the O_3 concentrations that would produce a trace (5 percent) of foliar injury at various time intervals (Figure 6-5; Table 6-14). The limiting values shown in Figures 6-3 and 6-4 were developed from a review of the literature available at that

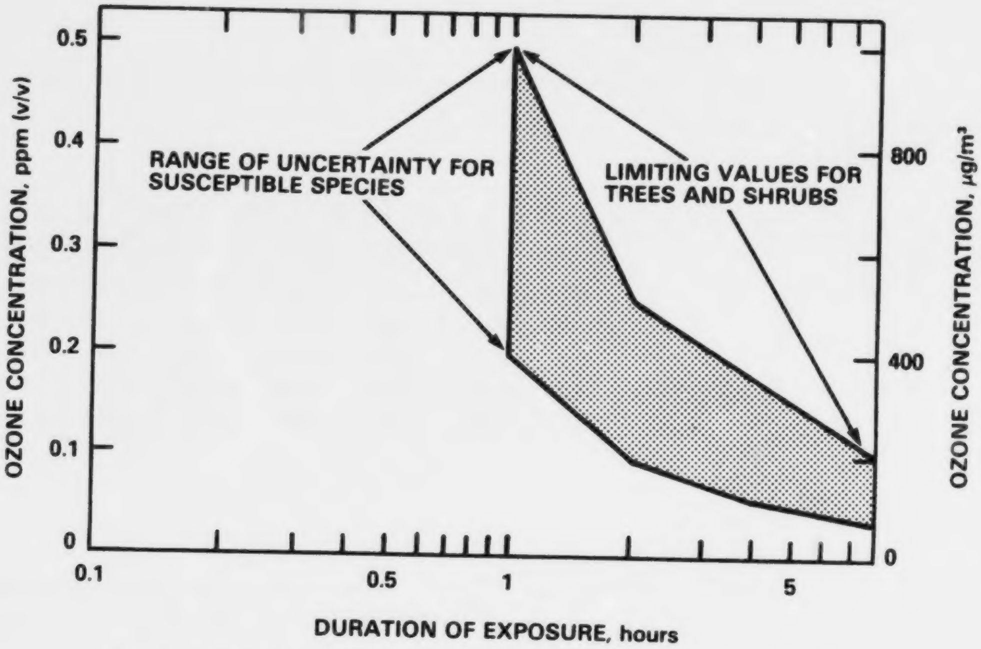


Figure 6-3. Limiting values for foliar injury to trees and shrubs by ozone.

Source: U.S. Environmental Protection Agency (1978).

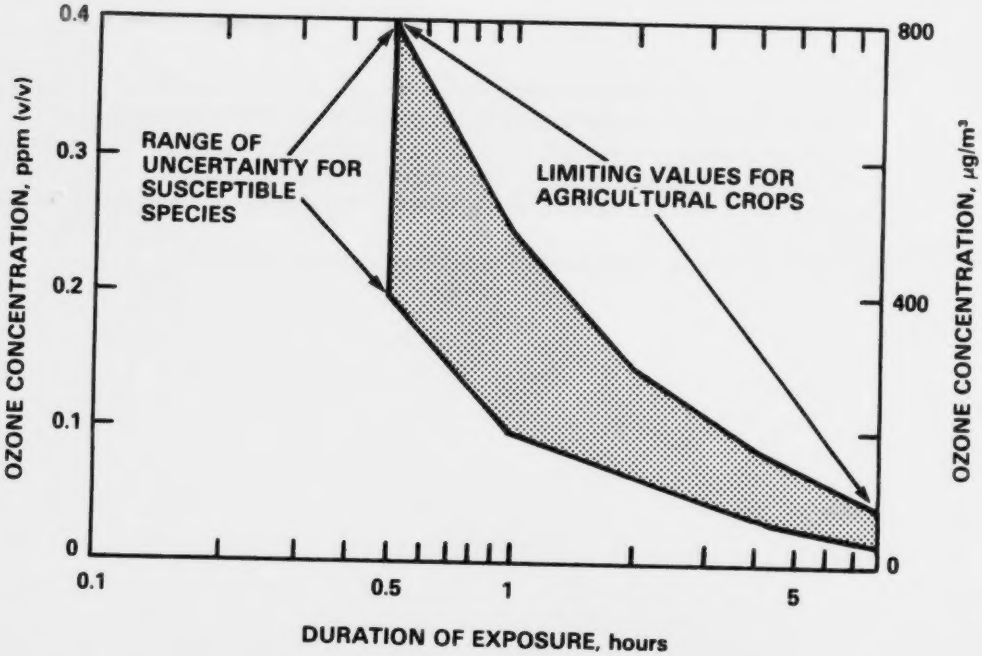
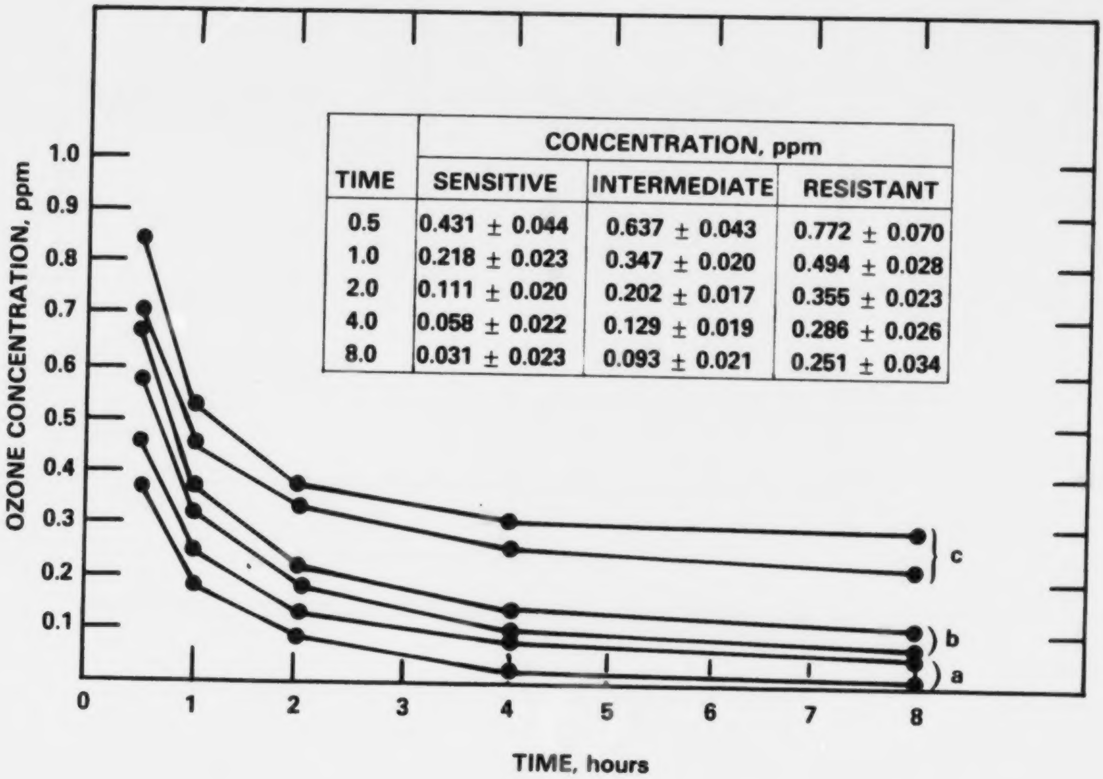


Figure 6-4. Limiting values for foliar injury to agricultural crops by ozone.

Source: U.S. Environmental Protection Agency (1978).



TIME	CONCENTRATION, ppm		
	SENSITIVE	INTERMEDIATE	RESISTANT
0.5	0.431 ± 0.044	0.637 ± 0.043	0.772 ± 0.070
1.0	0.218 ± 0.023	0.347 ± 0.020	0.494 ± 0.028
2.0	0.111 ± 0.020	0.202 ± 0.017	0.355 ± 0.023
4.0	0.058 ± 0.022	0.129 ± 0.019	0.286 ± 0.026
8.0	0.031 ± 0.023	0.093 ± 0.021	0.251 ± 0.034

Figure 6-5. Ozone concentrations versus duration of exposure required to produce 5 percent foliar injury in plants of three different sensitivity groupings. The curves were generated by developing 95 percent confidence limits around the equations for all plants in each susceptibility grouping from Table 6-14. Curves: a = sensitive plants, b = intermediate plants, c = resistant plants.

Source: U.S. Environmental Protection Agency (1978).

TABLE 6-14. CONCENTRATION, TIME, AND RESPONSE EQUATIONS FOR THREE SUSCEPTIBILITY GROUPS AND FOR SELECTED PLANTS OR PLANT TYPES WITH RESPECT TO OZONE[a]

Plants	$(C = A_o + A_t I + A_2 T)$[b]			R^2[c]	Threshold concentration, ppm[d] 1 hr	4 hr	8 hr	Number data points	Mean values[e] Conc. (C), ppm	Time (T), hr	Response (I), %	Dose, ppm x hr
Sensitive:												
All plants	-0.0152	+0.00401	+0.213/T	0.57	0.22	0.06	0.03	471	0.29	1.74	45.4	0.503
Grasses	-0.0565	+0.00481	+0.291/T	0.74	0.26	0.04	0.01	71	0.37	1.66	50.9	0.608
Legumes	0.0452	+0.00361	+0.172/T	0.46	0.24	0.11	0.09	100	0.34	1.42	40.1	0.480
Tomato	-0.0823	+0.00431	+0.243/T	0.50	0.18	None	None	20	0.31	1.50	56.5	0.491
Oat	-0.0427	+0.00511	+0.273/T	0.76	0.26	0.05	0.02	30	0.37	1.66	40.2	0.611
Bean	-0.0090	+0.00301	+0.164/T	0.58	0.17	0.05	0.03	62	0.30	1.23	47.2	0.370
Tobacco	0.0245	+0.00341	+0.137/T	0.52	0.18	0.08	0.06	197	0.23	1.90	38.9	0.448
Intermediate:												
All plants	0.0244	+0.00651	+0.290/T	0.74	0.35	0.13	0.09	373	0.37	1.67	27.0	0.625
Vegetables	-0.0079	+0.00641	+0.263/T	0.79	0.29	0.09	0.06	25	0.41	1.29	33.5	0.532
Grasses	0.0107	+0.00591	+0.292/T	0.82	0.33	0.11	0.09	68	0.39	1.61	31.0	0.625
Legumes	0.0116	+0.00741	+0.329/T	0.81	0.38	0.13	0.09	104	0.40	1.59	25.0	0.642
Perennial	0.0748	+0.00701	+0.237/T	0.77	0.35	0.17	0.14	27	0.36	1.91	22.9	0.687
Clover	-0.0099	+0.00711	+0.268/T	0.95	0.29	0.09	0.06	24	0.28	2.13	23.0	0.595
Wheat	-0.0036	+0.00811	+0.302/T	0.88	0.34	0.11	0.08	15	0.47	1.25	28.9	0.508
Tobacco	0.0631	+0.00871	+0.152/T	0.78	0.26	0.14	0.13	59	0.28	1.99	15.7	0.551
Resistant:												
All plants	0.1689	+0.00951	+0.278/T	0.51	0.50	0.27	0.25	291	0.45	1.55	10.6	0.696
Legumes	0.0890	+0.01081	+0.304/T	0.82	0.45	0.22	0.18	36	0.30	1.89	12.2	0.722
Grasses	0.1906	+0.01171	+0.263/T	0.55	0.51	0.31	0.20	13	0.45	1.47	6.5	0.655
Vegetables	0.1979	+0.01261	+0.107/T	0.70	0.38	0.29	0.20	16	0.55	1.50	17.8	0.819
Woody plants	0.2312	+0.00611	+0.208/T	0.45	0.47	0.31	0.30	46	0.39	2.50	7.8	0.905
Cucumber	0.1505	+0.01411	+0.106/T	0.83	0.33	0.25	0.23	18	0.41	1.41	13.3	0.581
Chrysanthemum	0.2060	+0.00521	+0.256/T	0.40	0.49	0.30	0.27	45	0.39	2.17	12.6	0.847

[a] Equations were developed from exposures limited in time (0.5 to 8 hr except for 2 to 12 hr points in the sensitive group) and denote acute responses of the plants. Concentrations range from 0.05 to 0.99 (1.0) ppm and responses from 0 to 99 (100)% of control.

[b] C is ozone concentration in ppm, I is percent injury, T is time in hr, and A_o, A_t, and A_2 are constants (partial regression coefficients) that are specific for pollutant plant species or group of species, and environmental conditions used.

[c] Multiple correlation coefficient squared, which represents the percent variation explained by the model.

[d] For 5 percent response in 1-, 4-, and 8-hr periods.

[e] From the computer analysis.

Source: U.S. Environmental Protection Agency (1978.)

time (1976) and represented the lowest concentration and time reported to cause visible injury on various plant species. These data were based on more than 100 studies of agricultural crops and 18 studies of tree species. In the figures, the shaded areas represented the range of uncertainty in the data. Foliar injury was considered unlikely at doses below and to the left of the shaded areas. The limiting values were summarized as follows:

1. Agricultural crops:
   a. 0.20 to 0.41 ppm for 0.5 hr.
   b. 0.10 to 0.25 ppm for 1.0 hr.
   c. 0.04 to 0.09 ppm for 4.0 hr.

2. Trees and shrubs:
   a. 0.20 to 0.51 ppm for 1 hr.
   b. 0.10 to 0.25 ppm for 2 hr.
   c. 0.06 to 0.17 ppm for 4 hr.

A concept similar to the limiting values for foliar injury was developed to present the O_3 concentrations and durations which could potentially reduce plant growth and yield (Figure 6-6). In the figure, the line displays the boundary of mean O_3 concentrations and exposure durations below which effects on growth and yield were not observed. Most of the data points represented effects on growth rather than on yield as defined in the present document (see Section 6.2.5). The graphical analysis indicated that the lower limit for effects was a mean O_3 concentration of 0.05 ppm for exposure durations greater than 16 days. At exposure durations of less than 16 days, the O_3 response threshold increased to about 0.10 ppm at 10 days and 0.30 ppm at 6 days.

In the sections that follow, greater emphasis will be placed on yield loss rather than just injury. Visible foliar injury will be considered for those plants in which the foliage is the marketable plant part (yield), for plants used for aesthetic purposes, and for plants used as bioindicators.

In the following portions of Section 6.4, the use of plants as bioindicators and effects on vascular and nonvascular plants will be discussed. Bioindicators are important, because they provide useful information about locations displaying potential O_3 impacts and may be useful in elucidating O_3 as a causative factor in yield loss.

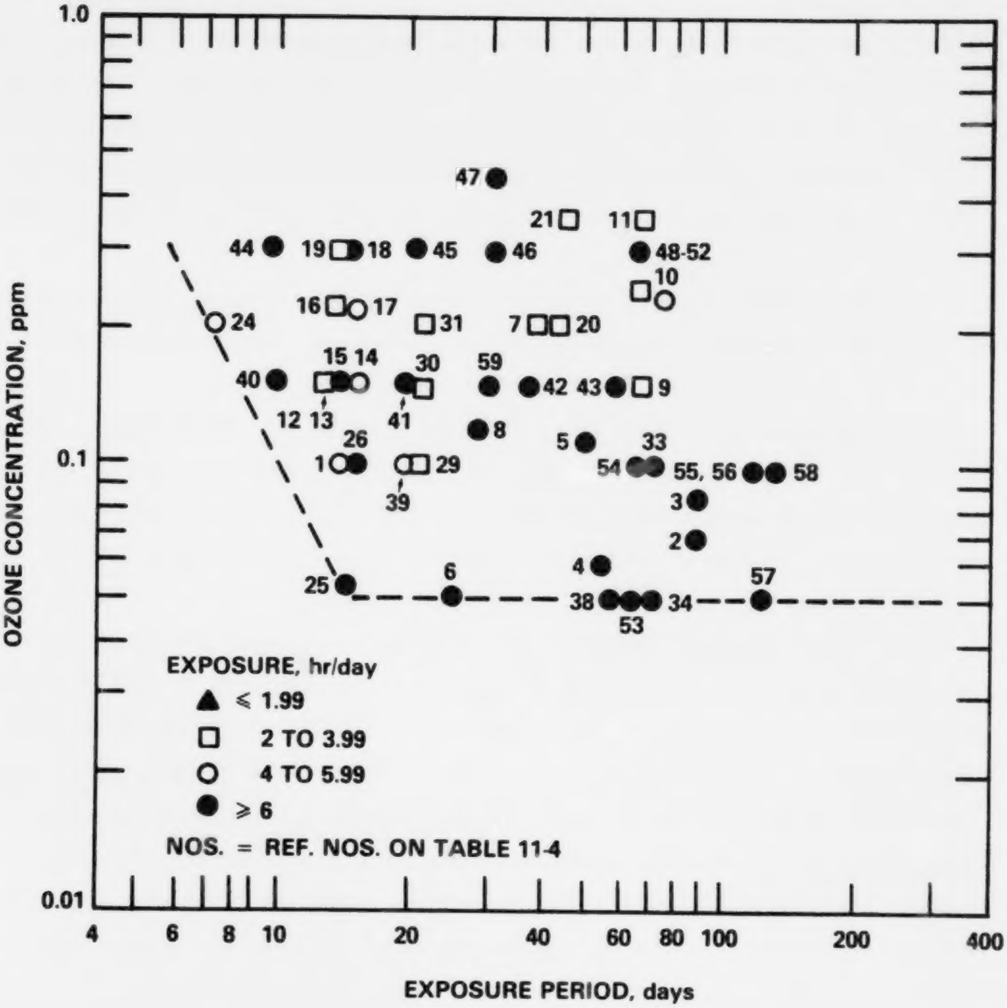


Figure 6-6. Relationship between ozone concentration, exposure duration, and reduction in plant growth or yield (see Table 6-18). Numbers on the figure refer to reference numbers in Table 11-4, U.S. Environmental Protection Agency (1978).

Source: Derived from National Research Council (1977); cited in U.S. Environmental Protection Agency (1978).

6.4.1 Bioindicators of Ozone Exposure

Plants are known to respond differentially to the characteristics of the environments that they occupy (Treshow, 1980b). Temperature, moisture, solar radiation, elevation, and soil quality are obvious environmental features that affect the distribution and relative performance of vegetation. Because established plants are confined to a particular location, they depend primarily on that local environment to meet their requirements for growth and reproduction; therefore, plant growth and yield integrate all environmental factors. Thus, vegetation can act as a biological indicator of the environment, which includes air pollutants.

Because plants growing in a particular environment are integrated products of that environment, they can provide important information about air pollution effects. The response if a plant is the direct expression of the pollutant in tion occurrence and magnitude (Laurence, 1984). Therefore, bioindicators provide a direct method for understanding the risk that pollution presents to the biological components of the affected environment (Guderian, 1977). For this reason, there is renewed interest in biological methods for determining air pollution effects (Manning and Feder, 1980).

6.4.1.1 Bioindicator Methods. As the use of plants to monitor air pollution has increased, better methods have been developed for relating plant response to pollution exposure. Manning and Feder (1980) have summarized the important attributes of a bioindicator species. To perform predictably, the plants should be sensitive to a specific pollutant, genetically uniform, native or adaptable to the region, produce characteristic symptoms, grow indeterminately, and respond proportionally to pollutant exposure. To minimize sources of variation further, efforts should be made to provide uniform soil and water conditions and to ensure observation by trained personnel (Oshima et al., 1976; Posthumus, 1976, 1980). The aim of these measures is to standardize the plant and growing conditions so that effects of the pollutant are the major sources of variation in the subsequent analysis (Teng, 1982). During the past 10 years, substantial progress has been made toward improved understanding of the variables affecting the performance of indicator species. Specific examples of these studies are summarized in this section.

6.4.1.2 Response of Indicator Species. Early studies with indicator species generally focused on visible symptoms, the most obvious reaction of a plant to changes in its environment. These responses included chlorosis or necrosis of tissues and typically represented the effects of an acute exposure to a single pollutant (Feder and Manning, 1979; Heck, 1966; Heggestad and Darley, 1969; Laurence, 1984). The identification and application in the 1960s of very sensitive species such as Bel W-3 tobacco (Heggestad and Menser, 1962) provided predictive means by which to identify exposures to progressively lower concentrations of O_3 (Feder, 1978). There is general agreement that this tobacco cultivar will predictably respond to an O_3 exposure above 0.04 ppm for 4 hr (Ashmore et al., 1978) when environmental conditions are favorable.

Broad-leaved (dicotyledonous) and narrow-leaved (monocotyledonous) plants show different symptoms from exposure to O_3. The foliage of dicotyledonous plants initially appears water-soaked as the result of injury to palisade cell membranes (U.S. Environmental Protection Agency, 1976). These areas appear shiny or oily within hours of the exposure and have characteristic flecks or stipples when the water-soaked area dries (Figure 6-7). Flecks (Figure 6-8) are small lesions formed when groups of palisade or mesophyll cells, or both, die and the associated epidermal cells collapse (U.S. Environmental Protection Agency, 1976). They may be yellow or tan; and if the injury is extensive the entire leaf surface may appear bronzed. Individual flecks may coalesce to form bifacial lesions that appear on both leaf surfaces. "Stipples" (Figure 6-7) are small groups of red, purple, or black pigmented palisade cells (U.S. Environmental Protection Agency, 1976) that can be seen through the uninjured epidermal layer of the upper leaf surface. The leaf veins are also uninjured and form angular boundaries to the pigmented areas.

Monocotyledonous plants generally do not have differentiated mesophyll tissue, and ozone injury typically appears as chlorotic spots or white flecks between veins (U.S. Environmental Protection Agency, 1976). This injury may extend to form long white or yellow streaks between the parallel veins of sensitive plants, which become, in their most severe form, leaf bands (Figure 6-9).

Ozone injury to the foliage of coniferous plants is described as chlorotic mottle and tipburn (U.S. Environmental Protection Agency, 1976). Small patches of needle tissue are injured and turn yellow. These areas are surrounded by healthy green tissue so that the needle appears mottled (Figure 6-10). When the entire needle tip dies, it first turns reddish brown and then gray. Tipburn is also a characteristic of O_3 injury. In both cases, it is usual for only current-year needles to be affected after acute exposures to O_3.

Long-term exposure to low pollutant concentrations may adversely affect plant health without producing visible symptoms. Chronic injury from this type of exposure may be represented by reductions in growth or yield, or both;

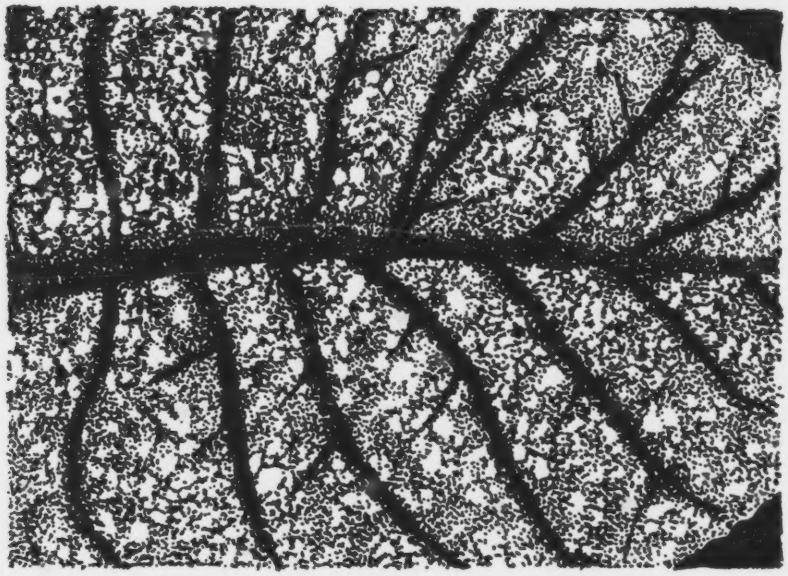


Figure 6-7. Ozone injury to Bel W-3 tobacco. Clear interveinal areas represent necrotic tissue (fleck and bifacial necrosis).

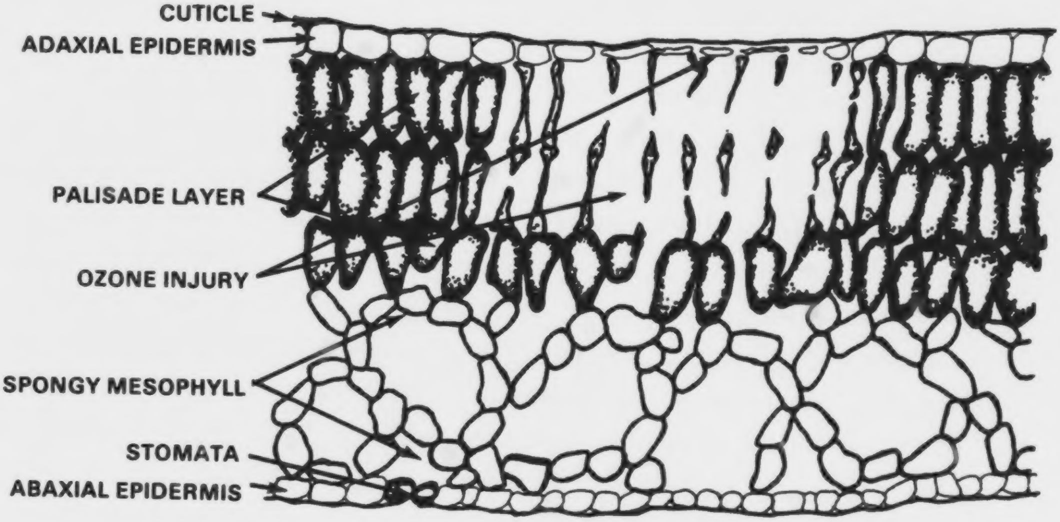

CUTICLE
ADAXIAL EPIDERMIS
PALISADE LAYER
OZONE INJURY
SPONGY MESOPHYLL
STOMATA
ABAXIAL EPIDERMIS

Figure 6-8. Schematic cross section of typical dicot leaf showing ozone injury to palisade cells and collapsed epidermal cells.

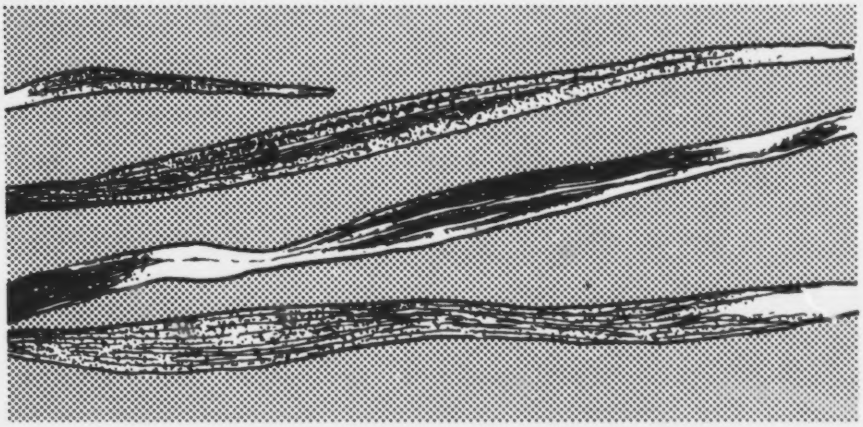


Figure 6-9. Ozone injury to oats. Clear areas represent bleached and necrotic tissue.

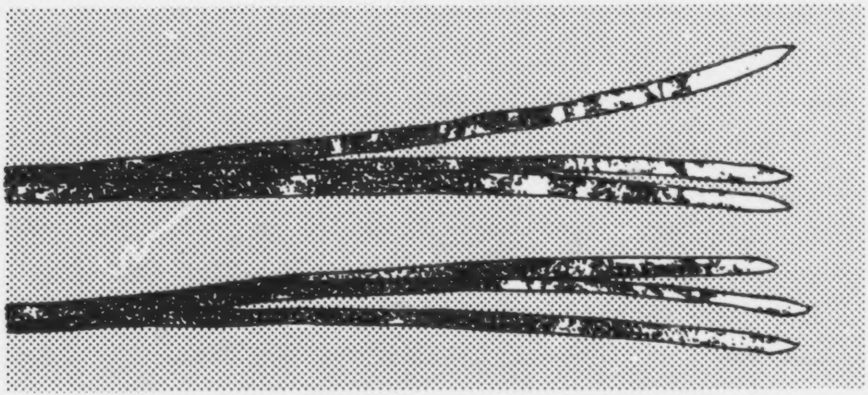


Figure 6-10. Ozone injury to conifer needles. Clear areas represent injured tissue (chlorotic mottle and tipburn).

or by premature defoliation resulting from changes in photosynthesis, respiration, leaf chlorophyl content, or other processes (Dochinger et al., 1970; Feder, 1978; Heck, 1966; Laurence, 1984; Posthumus, 1976).

6.4.1.3 Bioindicator Systems. Although many field biologists have identified certain plants as indicators of pollutants, few have published documentation of the sensitivity of specific plants to ambient O_3 in the field or in natural environments. Duchelle and Skelly (1981) and Skelly et al. (1982) characterized the response of milkweed to O_3 in both field and laboratory studies. This is a particularly valuable study, because it defines the response of a plant that has been classed as a sensitive bioindicator in the field and establishes a baseline sensitivity that can be reevaluated in the future to detect possible changes in the frequency of sensitive individuals in the field. Benoit et al. (1982), reporting on the radial growth of eastern white pine as an indicator of O_3 pollution, were able to identify three classes of eastern white pine (sensitive, intermediate, and tolerant). Studies in the southern California mountains (Miller, 1973) showed that the radial growth of ponderosa and Jeffrey pines was an indicator of ambient O_3 exposure. Although a good relationship between radial growth and observed O_3 sensitivity exists, it is probably realistic to use this procedure only as a measure of long-term effects because it requires the detailed analyses of tree rings and precipitation patterns.

There have been several reports on the use of plants in systems designed to detect the presence of elevated concentrations of ozone. Many early studies (e.g., Heck, 1966) were conducted to assess the spatial and temporal distribution of air pollution using sensitive indicator plants. In most cases, poor correlations between measured oxidants and plant injury were found. With the identification of Bel W-3 tobacco as a sensitive indicator of elevated ambient O_3 concentrations (Heggestad and Menser, 1962), a new series of studies was conducted (e.g., Heck et al., 1969, Heck and Heagle, 1970; Jacobson and Feder, 1974; Naveh et al., 1978; Goren and Donagi, 1979; Horsman, 1981; Ashmore et al., 1978; 1980; Bell and Cox, 1975). The most widespread network established to determine the spatial and temporal distribution of ambient-oxidant-induced injury on Bel-W3 tobacco was that described by Jacobson and Feder (1974). The bioindicator sites were located in nine states ranging from North Carolina to Maine. The authors observed both temporal and spatial variations in O_3 injury and concluded that Bel-W3 could be used to indicate the present of O_3 but could not reliably indicate the O_3 concentration. A major problem identified by the authors was the necessity of growing Bel W-3 plants under pollution-free conditions prior to their use.

Oshima (1974) devised a bioindicator system for use in California that utilized pinto bean. In field trials, a strong and significant relationship was found between injury observed on bean leaves and average weekly ambient O_3 dose. His measure of O_3 dose consisted of a censored sum (hours greater than 0.1 ppm) of ambient O_3 concentrations obtained from nearby physical monitors. It would be feasible to use such a system on a large scale to assess, at least qualitatively if not quantitatively, the spatial and temporal occurrence of phytotoxic concentrations of O_3.

Posthumus (1976) reported the results of a study to investigate the occurrence and distribution of O_3 by using Bel W-3 tobacco at 31 sites throughout the Netherlands. He reported, "It is possible to determine the place and time with the highest mean intensity or highest frequency of injury by O_3...". A "'fingerprint'" can be produced and, by comparing patterns from year to year, specific trends in the occurrence of pollution may be identified. He further concluded that, "The clear advantage of plants as indicators of air pollution is that these show the result of the action of the pollutants on living material", and added that, "In this way it could be a rather efficient and relatively inexpensive manner to follow trends in air pollution and to evaluate sanitation measures."

Nouchi and Aoki (1979) used morning glory as an indicator of photochemical oxidants (primarily O_3). In studies conducted both in the laboratory and field, they were able to model the effects of O_3 on leaf injury, including the effects of previously occurring exposures. Field verification of their model showed that they were able to determine (within acceptable margins of error) oxidant levels on a given day by using measurements of visible injury to morning glory. They emphasized, however, that the most valuable use of their system was to characterize the frequency and spatial distribution of elevated oxidant concentrations.

The common theme in all these studies is that a good understanding of the occurrence of elevated O_3 concentrations can be obtained by using the visible response of sensitive plants. While the methodology for biomonitoring is still in the early stages of development, bioindicators have a certain value as integrators, by providing information on where, when, and how often O_3 concentrations may be reaching phytotoxic concentrations. The value of deploying networks of bioindicators has been demonstrated in the early detection of developing regional oxidant pollution problems, in the identification of trends in pollutant occurrence, and in the supplementation of physical monitoring networks to provide additional information on the biological effects of pollution for the assessment of crop loss (Laurence, 1984).

Following the initial observations that plants exhibited foliar injury after exposure to ambient oxidants, studies were undertaken to determine the concentrations and spatial distribution of ozone based on the appearance of visible foliar injury symptoms (e.g., Heck et al., 1969). Although there has been no single study to determine whether ozone injures vegetation in every state in the country, a number of studies (using varying degrees of detail) have identified ozone injury on a diverse range of vegetation (Table 6-15). Based on the occurrence of foliar injury, ozone impacts have been observed on horticultural and agricultural crops, native vegetation, and bioindicator plants (Table 6-15; Figure 6-11) in at least 27 states. Because comprehensive studies of the distribution of ozone injury have not been conducted, it is not possible to determine whether ozone injury does not occur in the other states or whether it has not been reported because it has not been studied.

Biological methods for assessing the extent, and in some cases the intensity, of O_3 effects have value beyond the data provided by physical-chemical monitoring methods. The physical-chemical methods can describe the concentration and duration of exposure and can only show the probability that an effect may have occurred. In contrast, vegetation (bioindicators) can provide direct indication that the pollution episode reached injurious levels, subject to the joint influence of other environmental variables. Although the presence of visible foliar symptoms on vegetation cannot be directly related to effects on plant growth or yield, they do indicate that elevated levels of O_3 have occurred. The detection of visible symptoms is an indication that additional studies should be undertaken to determine whether effects on plant growth and yield are occurring. Caution should be used when relying on visible symptoms, however, because the lack of foliar injury is not proof that effects on growth are not occurring.

6.4.2 Response of Microorganisms and Nonvascular Plants to Ozone

6.4.2.1 Microorganisms.

Most studies with this group of organisms (bacteria and fungi) have often used O_3 concentrations in excess of 1 ppm, much higher than those expected to occur in ambient air. Direct effects of ozone on microorganisms and, in some instances, their capacity to incite plant diseases

TABLE 6-15. PARTIAL LISTING OF STATES WHERE AMBIENT OZONE INJURY HAS BEEN OBSERVED ON SENSITIVE VEGETATION

State	Horticultural crops	Agricultural crops	Natural vegetation	Bioindicator	Reference
Arizona				Tobacco	National Research Council (1977)
California	Ginkgo	Tomato, grapes, cotton, citrus, sweet corn, potato	Ponderosa pine, Jeffrey pine, 5 other pine species, black oak, and 11 herbaceous species	Pinto bean, alfalfa, grapes	Seibert (1970); Oshima (1974b); Oshima et al. (1976); Oshima et al. (1977a); Richards et al. (1958); Brewer and Ferry (1974); Thompson et al. (1969); Foster et al. (1983a); Miller and Elderman (1977); Williams et al. (1977)
Connecticut	Petunia	Tobacco, alfalfa, beans, tomato, potato, cucurbits, oats, 6 vegetables		Tobacco	Jacobson and Feder (1974); Heggestad and Middleton (1959); Rich et al. (1969)
Delaware		Potato		Tobacco	Jacobson and Feder (1974); Brasher et al. (1973)
Florida				Tobacco	Dean (1963)
Georgia	Petunia			Tobacco	Walker and Barlow (1974)
Illinois		Soybean			
Indiana			White pine		Kress and Miller (1983) Usher and Williams (1982)
Kentucky				Tobacco	Menser (1969)
Maine				Tobacco	Jacobson and Feder (1974)
Maryland		Soybean, snap bean, and potato	Sycamore	Tobacco	Santamour (1969); Howell et al. (1979); Heggestad (1973); Heggestad et al. (1980)
Massachusetts		Potato		Tobacco	Jacobson and Feder (1974); Manning et al. (1969)
Michigan		Potato, field bean, bean		Tobacco	Hooker et al. (1973); Olson and Saettler (1979)
Minnesota		Soybean			Laurence et al. (1977)
Missouri				Tobacco	Heck et al. (1969)

TABLE 6-15 (cont'd). PARTIAL LISTING OF STATES WHERE AMBIENT OZONE INJURY HAS BEEN OBSERVED ON SENSITIVE VEGETATION

State	Horticultural crops	Agricultural crops	Natural vegetation	Bioindicator	Reference
New Jersey	Austrian pine, petunia, sweet pea, and carnation	Potato, spinach, cucurbits, cereals, grape, broccoli, alfalfa, 10 other vegetables	Chickweed, orchard grass, red clover, and pine	Tobacco	Jacobson and Feder (1974); Harkov and Brennan (1982); Clarke and Brennan (1981); Daines (1963); Daines et al. (1967); Pell (1973)
New York		Tomato, bean, grape, soybean		Tobacco	Jacobson and Feder (1974); MacLean and Schneider (1976); Kender et al. (1973); Troiano et al. (1983)
North Carolina		Snap bean, soybean, spinach, field corn, winter wheat		Tobacco	Jacobson and Feder (1974); Heggestad et al. (1980); Heagle and Heck (1980)
Ohio	Petunia	Bean, radish, squash, tomato, alfalfa, oats	Eastern white pine	Tobacco	Heck and Heagle (1970); Dochinger and Seliskar (1970); Reinert et al. (1970)
Pennsylvania	Austrian pine, mimosa, white oak, dogwood, hemlock, silver maple, bluegrass, 21 additional trees	Alfalfa, corn, oats, tomato, sugar beets, beans, grape, spinach, broccoli, Swiss chard, 9 additional crops	White pine, spruce, blackberry, blueberry, poison ivy, nightshade, chickweed, and 7 additional species	Tobacco	Jacobson and Feder (1974); Seibert (1970); Moyer et al. (1974); Lacasse (1971)
South Dakota				Tobacco	Gardner (1973)
Tennessee				Tobacco	Menser (1969)
Utah	Petunia	Barley, oats, spinach, corn, radish		Tobacco	Tingey and Hill (1967)
Virginia		Potato	Tulip poplar, green ash, sweet gum, eastern white pine, 3 additional conifers, milkweed, wild strawberry, grasses, sedges, forbs		Duchelle and Skelly (1981); Heggestad (1973)
Washington				Tobacco	National Research Council (1977)
West Virginia			White pine		Wood and Pennypacker (1975)
Wisconsin		Onions	Pine		Usher and Williams (1982); Daines et al. (1967)

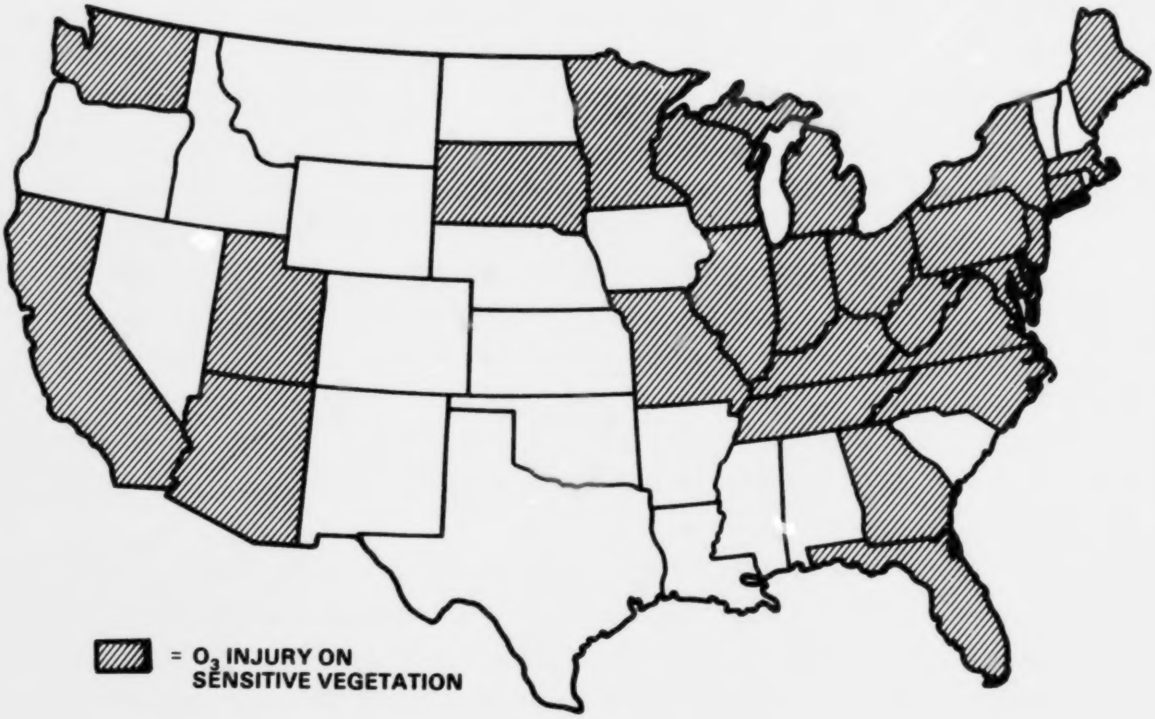

▨ = O$_3$ INJURY ON SENSITIVE VEGETATION

Figure 6-11. States in which ozone-induced injury to vegetation has occurred as reported in the published literature.

have been reviewed by Laurence (1981) and Heagle (1973, 1982), and in Section 6.3.2.1.3 in this chapter.

The O_3 concentration required for direct impact on microorganisms may be quite high. The data of Hibben and Stotsky (1969) are illustrative. These investigators examined the response of detached spores of 14 fungi to 0.1 to 1.0 ppm of O_3 for 1, 2, and 6 hr. The large pigmented spores of *Chaetomium* sp., *Stemphylium sarcinaeforme*, *S. loti*, and *Alternaria* sp. were not affected by 1.0 ppm. Germination of *Trichoderma viride*, *Aspergillus terreus*, *A. niger*, *Penicillium egyptiacum*, *Botrytis allii*, and *Rhizopus stolonifera* spores was reduced by O_3 exposure, but only at concentrations above 0.5 ppm. The germination percentages in the small colorless spores of *Fusarium oxysporum*, *Colletotrichum largenarium*, *Verticillium albo-atrum*, and *V. dahliae* were reduced by 0.5 ppm and occasionally by concentrations of 0.25 ppm of O_3 for 4 to 6 hr; lower doses stimulated spore germination in some cases. The ability of ozone to reduce spore germination in fungi apparently depends on the species, spore type, morphology, moisture, and substrate. Moist spores were more sensitive than dry ones; single-celled spores and those with thin cell walls were most sensitive.

Hibben and Stotsky (1969) found O_3 toxic to moist fungus spores of some species, even at concentrations of 0.1 ppm when applied for 28 hr. Exposure to 0.5 and 1.0 ppm reduced or prevented germination of spores of all species tested. Ozone at 0.1 ppm for 4 hr or at 1.0 ppm for 2 hr stopped apical cell division of conidiophores of *Alternaria solani* and caused collapse of the apical cell wall (Rich and Tomlinson, 1968).

Ozone can inhibit fungal growth on artificial media but rarely kills the fungus even at high concentrations. Differences in species sensitivity are known. In several fungi, exposure to O_3 (0.10 or 0.40 ppm for 4 hr) caused a 10- to 25-fold increase in sporulation (Heagle, 1973). The same author reported the effects of low O_3 exposures on three obligate parasitic fungi. Germination of spores was not affected in any of these studies (Heagle, 1975). Reduced sporulation, germination, and pathogenicity of *Botrytis cinerea* were observed by Krause and Weidensaul (1978a,b) after exposure of the microorganism *in vitro* and *in vivo* to 0.30 ppm of O_3 for two 6-hr periods.

6.4.2.2 *Lichens, Mosses, and Ferns*. Previously, there was little information describing the effects of O_3 on lichens in natural environments, but Sigal and Nash (1983) have recently conducted an extensive study of lichen distribution relative to oxidant air pollution in southern California. Collections of lichen from regions of high (1300 hr > 0.09 ppm, 1968-1974, San Bernardino Mountains) and low (Cuyamaca Rancho State Park) levels of oxidant pollution were compared with collections made in 1913. The frequency and cover of the current lichen communities in these regions were also compared with calculated levels of O_3 associated with injury to pines as reported earlier (National Research Council, 1977). Additionally, lichens from unaffected areas were transplanted to ecologically similar sites in affected areas.

In this multisite study, the authors found consistently high levels of injury to lichens in areas with high levels of O_3. In polluted areas, only 8 of 16 previously reported species were still present, and 4 were found only in trace amounts. This compared with 15 of 16 species still present in areas with low levels of O_3. Transplanted lichens performed poorly in areas where injury to pine was most extensive and calculated levels of O_3 were highest. The authors concluded that lichen communities in southern California were not adversely affected if the cumulative oxidant dose level was below about 300 ppm-hr per year. This dose was calculated using all concentrations greater than 0.04 ppm O_3.

In a laboratory study, Nash and Sigal (1979) fumigated two species of lichens (Parmelia sulcata and Hypogymnia enteromorpha) with O_3 at concentrations of 0.5 and 0.8 ppm for 12 hr. The former exhibited greater sensitivity than the latter, as measured by a reduction in gross photosynthesis. P. sulcata, which grows on black oak, is absent from the San Bernardino Mountains; H. enteromorpha is present but apparently deteriorating. The authors noted that, for these species, the pattern observed in the laboratory is consistent with that found in field observations in Southern California, where extensive O_3 injury occurs. In another study (Ross and Nash, 1983), photosynthesis was decreased at O_3 concentrations of 0.1, 0.25, and 0.50 ppm for 12 hr in Pseudo parmelia caperata; however, effects were not found when Ramalina menziesei was exposed to concentrations of O_3 up to 0.5 ppm for 12 hr. Exposures of both species to ozone at 0.10 ppm for 6 hr/day on 5 consecutive days resulted in the same responses seen at the higher concentrations.

Very little is known about the responses of mosses and ferns to O_3. The information in the previous EPA document (U.S. Environmental Protection Agency, 1978) indicates that, based on published information, significant effects would not be expected at current ambient O_3 levels.

6.4.3 Losses in Vascular Plants from Exposure to Ozone

This section will relate losses in plant yield to O_3 exposure. Exposures will be described in terms of duration and O_3 concentrations, but the statistics used to characterize the exposure will take several forms. Yield loss is defined as the impairment of the intended use of the plant (see Section 6.2.5) and includes aesthetic value, foliar injury, plant appearance, and losses in terms of number, size, or weight of the plant part that is normally harvested. Yield loss can also be defined as a change in physical appearance, chemical composition, or ability to withstand storage, traits that are collectively termed crop quality.

6.4.3.1 Losses in Aesthetic Value and Foliar Yield. Losses in aesthetic value are difficult, if not impossible, to quantify. For example, because of its aesthetic value, the loss of or adverse effects on a specimen tree or shrub in a landscape planting will result in a much greater economic loss than the same impact on a tree or shrub of the same or similar species growing as a part of a natural plant community. Foliar symptoms that can decrease the value of an ornamental crop may occur on various types of plants (e.g., turfgrasses, floral foliage, ornamental trees, and shrubs) with or without concomitant growth reductions. The occurrence of foliar injury on other crops in which the foliage is the marketable plant part (e.g., spinach, cabbage, tobacco) can substantially reduce marketability and constitute a yield loss in economic, if not biologic, terms.

Petunia, geranium, and poinsettia were exposed to O_3 (up to 0.10 to 0.12 ppm for 6 hr/day) for 9 days (petunia), 8 days (geranium), and 50 days (poinsettia) (Craker and Feder, 1972). Flower size was significantly reduced in all three species at a concentration of 0.10 to 0.12 ppm. Ozone decreased flower color in all three species: petunia (0.06 to 0.08 ppm), geranium (0.10 to 0.12 ppm), and poinsettia (0.02 to 0.04 ppm). All these changes in flower appearance (yield) occurred without visible injury to the plant leaves. Five begonia cultivars exposed to O_3 (0.25 ppm for 4 hr/day for a total of 16 hr over a 4-wk period) varied in foliar injury from 2 to 54 percent (Table 6-16); flower size was also reduced (Reinert and Nelson, 1980).

Ozone injury on the foliage of ornamental trees and shrubs impairs their appearance and may reduce their value. Mean foliar injury on eight azalea cultivars exposed to 0.25 ppm of O_3 (six 3-hr fumigations) ranged from 0 to 24 percent (Sanders and Reinert, 1982a). Stem weight was significantly reduced

TABLE 6-16. FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
FLOWERS							
Begonia (Schwabenland Red)	0.25	4 hr/day, every 6th day, 4 times	54 (39%[e] dec. in flower wt)	Chem	Not given	GH-CSTR	Reinert and Nelson (1980)
(Whisper 'O' Pink)	0.25		25 (22%[e] dec. in flower wt)				
(Fantasy)	0.25		2 (6%[e] dec. in flower wt)				
(Renaissance)	0.25		15 (55%[e] dec. in flower wt)				
(Turo)	0.25		8 (10% inc. in flower wt)				
ORNAMENTAL TREES AND SHRUBS							
Hybrid poplar (Dorskamp)	0.041	12 hr/day, 23 wk	Not given (1333%[e] inc. leaf drop)	Chem	NBKI	GH-CH	Mooi (1980)
(Zeeland)	0.041		Not given (692%[e] inc. leaf drop)				
Hinodegiri azalea	0.20	5 hr	33	Chem	NBKI	GC	Davis et al. (1981)
Black cherry	0.20		27				
American sycamore	0.20		26				
Hybrid poplar	0.20		20				

TABLE 6-16 (cont'd). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Yellow poplar	0.20	5 hr	19	Chem	NBKI	GC	Davis et al. (1981)
Black walnut	0.20		12				
Delaware Valley white azalea	0.20		12				
Black elder	0.20		11				
Spreading cotoneaster	0.20		4				
Austrian pine	0.20		0				
Eastern white pine	0.20		0				
Virginia pine	0.20		0				
Hinodegiri azalea	0.25	8 hr	95[f]	Chem	NBKI	GC	Davis and Coppolino (1974)
Korean azalea	0.25		70[f]				
Tree-of-heaven	0.25		65[f]				
Chinese elm	0.25		24[f]				
Mock-orange, sweet	0.25		17[f]				
Viburnum, tea	0.25		5[f]				
Viburnum, linden	0.25		2[f]				
American holly (♂)	0.25		0[f]				
American holly (♀)	0.25		0[f]				
Amur privet	0.25		0[f]				
Black gum	0.25		0[f]				
Dense Anglogap yew	0.25		0[f]				
Mountain-laurel kalmia	0.25		0[f]				
Hete Japanese holly	0.25		0[f]				

TABLE 6-16 (cont'd). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Hybrid poplar	0.25	12 hr/day, 24 days	Not given (50%[e] inc. in leaf abscission)	Chem	Known O_3 source	GH-CSTR	Noble and Jensen (1980)
Azalea (Red Wing)	0.25	3 hr/day, 6 days over 4 wk	1 (32%[e] dec. stem dry wt)	Chem	Known O_3 source	GH-CSTR	Sanders and Reinert (1982a)
(Snow)	0.25		0				
(Glacier)	0.25		24				
(Hersey Red)	0.25		21 (44%[e] dec. stem dry wt)				
(Pink Gumpo)	0.25		0				
(Mme. Pericat)	0.25		4				
(Red Luann)	0.25		8 (25%[e] dec. stem dry wt)				
(Mrs. G.G. Gerbing)	0.25		9				
TURFGRASS							
Turfgrass (Meyer zoysiagrass)	0.20	2 hr	0	Mast	Not given	CH	Richards et al. (1980)
(Tufcote bermudagrass)	0.20		0				
(Merion bluegrass)	0.20		0				
(Kenblue bluegrass)	0.20		2				
(K-31 tall fescue)	0.20		7				
(NK-100 ryegrass)	0.20		9				
(Penncross bentgrass)	0.20		14				
(Pennlawn red fescue)	0.20		17				
(Annual bluegrass)	0.20		20				

TABLE 6-16 (cont'd). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Kentucky bluegrass (Newport)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	0 5	Mast	Not given	CH	Richards et al. (1980)
(Sydsport)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	5 12				
(Merion)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	9 14				
(Fylking)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	9 14				
(Windsor)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	7 15				
(S. Dakota (certified))	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	10 17				
(Kenblue)	0.10	3.5 hr/day, 5 days 7 hr/day, 5 days	12 17				
Kentucky bluegrass (Adelphi)	0.15	6 hr/day, 10 days	6	UV	Not given	CH	Elkiey and Ormrod (1980)
(Baron)	0.15		0				
(Birka)	0.15		0				
(Cheri)	0.15		19				
(Fylking)	0.15		0				
(Merion)	0.15		9				
(Nugget)	0.15		8 (8% dec. in leaf area)				
(Plush)	0.15		0				
(Skofti)	0.15		0				
(Sydsport)	0.15		12				
(Touchdown)	0.15		0				

TABLE 6-16 (cont'd). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Kentucky bluegrass (Victa)	0.15	6 hr/day, 10 days	10	UV	Not given	CH	Elkiey and Ormrod (1980)
Red top (Common)	0.15		40				
Creeping bentgrass (Penncross)	0.15		20				
Colonial bentgrass (Exetes)	0.15		6				
Red fescue (Highlight)	0.15		2				
(Pennlawn)	0.15		6 (27%^{e} dec. in leaf area)				
Perennial ryegrass	0.15	11 (20%^{e} dec. in leaf area)					
FOLIAGE CROPS Tobacco	0.05	4 hr	0	Mast	NBKI	GH-CH	Tingey et al. (1973b)
(Bel B)	0.10		0				
(White Gold)	0.05 0.10		0 0				
Cabbage (All Season)	0.05 0.10		0 0				
Spinach (Northland)	0.05 0.10		0 0				
Spinach (America)	0.13	7 hr/day avg for 30 days (0.047 ppm O_3 ambient air each day)	49 (36%^{ng} dec. in fresh wt)	Chem	NBKI	OT	Heagle et al. (1979b)
(Winter Bloomsdale)	0.13		52 (45%^{ng} dec. in fresh wt)				
(Seven-R)	0.13		52 (55%^{ng} dec. in fresh wt)				
(Hybrid-424)	0.13		54 (42%^{ng} dec. in fresh wt)				
(Hybrid-7)	0.13		56 (43%^{ng} dec.) in fresh wt)				

TABLE 6-16 (cont'd). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Spinach (Viking)	0.13	7 hr/day avg for 30 days (0.047 ppm O_3 ambient air each day)	58 (44%[ng] dec. in fresh wt)	Chem	NBKI	OT	Heagle et al. (1979b)
(Dark Green Bloomsdale)	0.13		58 (58%[ng] dec. in fresh wt)				
(Viroflay)	0.13		60 (33%[ng] dec. in fresh wt)				
(Chesapeake)			63 (42%[ng] dec. in fresh wt)				
(Hybrid-612)	0.13		65 (61%[ng] dec. in fresh wt)				
(Dixie Market)	0.13		65 (55%[ng] dec. in fresh wt)				
Tobacco (GC-166)	Ambient air (Beltsville, MD)	11 wk	1	Mast	Not given	Field	Menser and Hodges (1972)
(CCC-E)			1				
(GC-172)			2				
(GC-169)			6				
(GC-18)			7				
(CCC-C)			10				
(GC-46)			10				
(CCC-L)			11				
(GC-50)			11				
(CCC-M)			15				

TABLE 6-16 (cont'd). FOLIAR SYMPTOM EXPRESSION OF VARIOUS FLOWER, ORNAMENTAL TREE, SHRUB, TURFGRASS, AND FOLIAR CROP SPECIES IN RESPONSE TO OZONE EXPOSURE[a]

Plant species	O_3 concn., ppm	Exposure duration	Percent foliar injury	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Tobacco (CCC-J)	Ambient air (Beltsville, MD)	11 wk	18	Mast	Not given	Field	Menser and Hodges (1972)
(CCC-S)			25				
(Bel-C)			55				

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[a] Where a column entry is blank, the information is as above.

[b] Chem = chemiluminescence; Mast = Mast oxidant meter (coulometric); UV = ultraviolet spectrometry.

[c] NBKI = neutral buffered potassium iodide.

[d] GH = greenhouse; GH-CSTR = continuous stirred tank reactor in a greenhouse; OT = open-top chamber; GC = growth chamber; CH = specially designed exposure chamber other than CSTR; GH-CH = exposure chamber in a greenhouse.

[e] Significant at P = 0.05; ng = not given.

[f] Severity index = [severity factor (0-5) x (% foliage injured) x (% population susceptible)] ÷ 100.

for three of the cultivars (Table 6-16). Tree and shrub species have developed foliar injury following exposure to 0.20 ppm of O_3 for 5 hr (Davis et al., 1981). Visible injury to black cherry foliage occurred following a 4-hr exposure at 0.10 ppm and 2 hr at 0.19 ppm of O_3 (Davis et al., 1981). In an earlier study, several species were exposed to O_3 (0.25 ppm for 8 hr) and evaluated for foliar injury (Davis and Coppolino, 1974). Some common ornamentals (holly, privet, yew, laurel, linden) exhibited no foliar injury, but others (azalea, tree-of-heaven, elm) appeared to be relatively sensitive (Table 6-16).

For ornamental tree plantings, excessive leaf drop decreases the value and thus can be considered a yield loss. Ozone has been shown to induce significant defoliation in hybrid poplar. Mooi (1980) noted increases of about 7- and 13-fold in leaf drop of two poplar cultivars exposed to 0.041 ppm, 12 hr/day, for 23 wk (Table 6-16). Noble and Jensen (1980) reported a 50 percent increase in leaf drop of hybrid poplar exposed to 0.25 ppm of O_3, 12 hr/day, for 24 days (Table 6-16).

Species and cultivars of turfgrass have exhibited foliar injury when exposed to 0.15 ppm of O_3 (6 hr/day, 10 days) (Elkiey and Ormrod, 1980). The extent of foliar injury was usually greater than the resultant growth inhibition. Ozone concentrations of 0.10 ppm for 3.5 hr/day for 5 days or 0.20 ppm for 2 hr were high enough to elicit injury in most turf grasses (Richards et al., 1980) (Table 6-16).

The appearance of the foliage on crops such as tobacco and spinach is important to the value of these crops and may affect their marketability. Tobacco and spinach failed to exhibit visible injury after exposure to 0.05 or 0.10 ppm of O_3 for 4 hr (Tingey et al., 1973b) (Table 6-16). In a different study, 11 spinach cultivars exhibited 49 to 65 percent mean foliar injury (and 33 to 61 percent mean fresh weight reduction) when exposed in the field to a 7-hr seasonal mean O_3 concentration of 0.13 ppm (Heagle et al., 1979b) (Table 6-16). The physical appearance of cigar-wrapper tobacco leaves may be very important to their value. Foliar injury from O_3 has been documented in the field (some cultivars are commonly used as bioindicators) and in controlled fumigations. In the field, plants of commercial tobacco cultivars grown in ambient air at Beltsville, MD, exhibited 1 to 55 percent O_3 injury (Menser and Hodges, 1972) (Table 6-16). Ozone concentrations of 0.10 ppm for 2 hr induced up to 20 percent foliar symptoms in controlled environment studies.

The above data are examples of O_3-induced impairments in the appearance and aesthetic value of plants as the result of foliar injury. Such effects occur at concentrations as low as 0.041 ppm for several weeks or 0.10 ppm for 2 hr, and these effects can constitute a yield loss when marketability of the plants is decreased. The actual amount of yield loss due to decreased aesthetic value or appearance may be more difficult to quantify than yield loss in weight or bulk.

6.4.3.2 Yield Losses as Weight, Size, and Number. The previous criteria document (U.S. Environmental Protection Agency, 1978) summarized the effects of acute and chronic O_3 exposures, with the primary focus on plant growth and a few reports that specifically studied yield loss (Tables 6-17, 6-18). Growth and yield reductions were observed in a diverse range of plant species at various exposure durations and O_3 concentrations. The majority of the studies were conducted in greenhouse or controlled-environment chambers, with only a few studies conducted in the field. These data indicated that as the exposure duration increased, the mean O_3 concentrations at which growth effects occurred decreased. When the exposure duration exceeded 15 days (not continuous exposures), mean O_3 concentrations of 0.05 ppm and greater caused significant growth and yield reductions. In field studies, significant growth and yield reductions were observed in commercial varieties of sweet corn, soybean, and pine seedlings (Heagle et al., 1972; Heagle et al., 1974; Wilhour and Neely, 1977) when the seasonal 6-hr O_3 concentration was 0.10 ppm or greater. In another field study, significant growth and yield reductions occurred in alfalfa when the 7-hr seasonal mean O_3 concentration was 0.05 ppm or greater (Neely et al., 1977).

In the following sections, yield losses are summarized in terms of weight or size and decrease in number from studies in which known amounts of O_3 were added to either charcoal-filtered or ambient air. The effects of ambient O_3 on yield are also presented.

6.4.3.2.1 Ozone addition studies. Ozone-induced yield-loss studies have used a variety of experimental approaches. Some studies have attempted to approximate typical agronomic conditions, and others have deviated from typical field practices in an attempt to have better control of the experimental conditions. Open-top chamber data will be discussed first, because most of these studies attempted to follow typical field practices. Results from

TABLE 6-17. EFFECTS OF SHORT-TERM EXPOSURES ON GROWTH AND YIELD OF SELECTED PLANTS[a]

Plant species	Ozone concentration, ppm	Exposure time, hr	Plant response, % reduction from control[b]
Begonia, cultivar White Tausendschon	0.10	2	5, avg. of 3 growth responses: shoot wt, flower wt, flower no.
	0.20	2	10, avg. of same responses
	0.40	2	19, avg. of same responses
	0.80	2	38, avg. of same responses
Petunia, cultivar Capri	0.10	2	9, avg. of same responses
	0.20	2	11, avg. of same responses
	0.40	2	21, avg. of same responses
	0.80	2	31, avg. of same responses
Coleus, cultivar Scarlet Rainbow	0.10	2	2, avg. of same responses
	0.20	2	17, avg. of same responses
	0.40	2	24, avg. of same responses
	0.80	2	39, avg. of same responses
Snapdragon, cultivar Floral Carpet, mixture	0.10	2	0, avg. of same responses
	0.20	2	6, avg. of same responses
	0.40	2	8, avg. of same responses
	0.80	2	16, avg. of same responses
Radish, cultivar Cavalier Cherry Belle	0.25	3	36, top dry wt (Cavalier)
			38, root dry wt (Cherry Belle)
Radish	0.40	1.5(1)[c]	37, root dry wt
		1.5(2)[c]	63, root dry wt
		1.5(3)[c]	75, root dry wt
Cucumber, cultivar Ohio Mosiac	1.00	1	19, top dry wt (1% injury)
	1.00	4	37, top dry wt (18% injury)
Potato, cultivar Norland	1.00	4	0, tuber dry wt (no injury)
	1.00	4(3)[c]	30, tuber dry wt (injury severe)
Tomato, cultivar Fireball	0.50	1	15, plant dry wt (grown in moist soil)
	1.00	1	20, plant dry wt (grown in moist soil)
Tomato, cultivar Fireball	0.50	1	15, increase in plant dry wt (grown in dry soil)
	1.00	1	25, increase in plant wt (grown in dry soil)
Onion, cultivar Spartan Era	0.20	24	0, effect
	1.00	1	19, plant dry wt (no injury)
	1.00	4	49, plant dry wt
Tobacco, cultivar Bel W_3	0.30	2	48, chlorophyll content

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[a] Taken from U.S. Environmental Protection Agency (1978).

[b] Unless otherwise noted.

[c] Number of exposures in parentheses.

TABLE 6-18. EFFECTS OF LONG-TERM, CONTROLLED EXPOSURES ON GROWTH, YIELD AND FOLIAR INJURY IN SELECTED PLANTS[a]

Plant species	Fig. 6-6[b] nos.	Ozone concentration, μg/m^3 (ppm)	Exposure time	Plant response, % reduction from control
Lemna, duckweed	1	196 (0.10)	5/day, 14 days	100, flowering; 36, flowering (1 wk after exposure completed)
				50, frond doubling rate
Carnation	2	98-177 (0.05-0.09)	24/day, 90 days	50, flowering (reduced vegetative growth)
Geranium	3	137-196 (0.07-0.10)	9.5/day, 90 days	50, flowering (shorter flower lasting time, reduced vegetative growth)
Petunia	4	98-137 (0.05-0.07)	24/day, 53 days	30, flower fresh wt
Poinsettia	5	196-235 (0.10-0.12)	6/day, 5 days/week, 10 weeks	39, bract size
Radish	6	98 (0.05)	8/day, 5 days/week, 5 weeks	54, root fresh wt 20, leaf fresh wt
		98 (0.05)	8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	63, root fresh wt 22, leaf fresh wt
Beet, garden	7	392 (0.20)	3/day, 38 days	50, top dry wt
Bean, cultivar Pinto	8	255 (0.13)	8/day, 28 days	79, top fresh wt 73, root fresh wt 70, height
Bean, cultivar Pinto	9	290 (0.15)	2/day, 63 days	33, plant wt; 46, pod fresh wt
	10	490 (0.25)	2/day, 63 days	95, plant dry wt; 99, pod fresh wt
	11	686 (0.35)	2/day, 63 days	97, plant dry wt; 100, pod fresh wt
Bean, cultivar Pinto	12	290 (0.15)	2/day, 14 days	8, leaf dry wt
	13	290 (0.15)	3/day, 14 days	8, leaf dry wt
	14	290 (0.15)	4/day, 14 days	23, leaf dry wt (data available on whole plants, roots, leaves, injury, and three levels of soil moisture stress)
	15	290 (0.15)	6/day, 14 days	49, leaf dry wt
	16	440 (0.225)	2/day, 14 days	44, leaf dry wt
Bean, cultivar Pinto	17	440 (0.225)	4/day, 14 days	68, leaf dry wt (data available on whole plants, roots, leaves, injury, and three levels of soil moisture stress)
	18	588 (0.30)	1/day, 14 days	40, leaf dry wt

TABLE 6-18 (cont'd). EFFECTS OF LONG-TERM, CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD AND FOLIAR INJURY IN SELECTED PLANTS[a]

Plant species	Fig. 6-6[b] nos.	Ozone concentration, μg/m³ (ppm)	Exposure time	Plant response, % reduction from control
	19	588 (0.30)	3/day, 14 days	76, leaf dry wt
Tomato	20	392 (0.20)	2.5/day, 3 days/week 14 weeks	1, yield; 32 top dry wt; 11, root dry wt
	21	686 (0.35)	2.5/day, 3 days/week, 14 weeks	45, yield; 72, top dry wt; 59, root dry wt
Corn, sweet, cultivar Golden Jubilee	22	392 (0.20)	3/day, 3 days/week till harvest	13, kernel dry wt; 20, top dry wt; 24, root dry wt
	23	686 (0.35)	3/day, 3 days/week till harvest	20, kernel dry wt; 48, top dry wt; 54, root dry wt
Wheat, cultivar Arthur 71	24	392 (0.20)	4/day, 7 days (anthesis)	30, yield
Soybean	25	98 (0.05)	8/day, 5 days/week 3 weeks	13, foliar injury
			8/day, 5 days/week (mixture of O_3 and SO_2 for same periods)	16, foliar injury 20, root dry wt
Soybean	26	196 (0.10)	8/day, 5 days/week 3 weeks	21, top dry wt 9, root dry wt
Alfalfa	27	196 (0.10)	2/day, 21 days	16, top dry wt
	28	290 (0.15)	2/day, 21 days	26, top dry wt
	29	390 (0.20)	2 day, 21 days	39, top dry wt
Grass brome	30	290-647 (0.15-0.33)(varied)	4/day, 5 days/week growing season	83, biomass
Alfalfa[c]	31	196 (0.10)	6/day, 70 days	4, top dry wt, harvest 1 20, top dry wt, harvest 2 50, top dry wt, harvest 3
Alfalfa[c]	32	98 (0.05)	7/day, 68 days	30, top dry wt, harvest 1 50, top dry wt, harvest 2
Alfalfa	33	98 (0.05)	8/day, 5 days/week 12 weeks	18, top dry wt
Pine, eastern white	34	196 (0.10)	4/day, 5 days/week 4 weeks (mixture of O_3 and SO_2 for same periods)	3, needle mottle (over 2-3 days of exposure) 16, needle mottle

TABLE 6-18 (cont'd). EFFECTS OF LONG-TERM, CONTROLLED OZONE EXPOSURES ON GROWTH, YIELD AND FOLIAR INJURY IN SELECTED PLANTS[a]

Plant species	Fig. 6-6[b] nos.	Ozone concentration, µg/m³ (ppm)	Exposure time	Plant response, % reduction from control
Pine, ponderosa	35	290 (0.15)	9/day, 10 days	4, photosynthesis
	36	290 (0.15)	9/day, 20 days	25, photosynthesis
Pine, ponderosa	37	290 (0.15)	9/day, 30 days	25, photosynthesis
	38	290 (0.15)	9/day, 60 days	34, photosynthesis
	39	588 (0.30)	9/day, 10 days	12, photosynthesis
	40	588 (0.30)	9/day, 20 days	50, photosynthesis
	41	588 (0.30)	9/day, 30 days	72, photosynthesis
	42	880-588 (0.30)	9/day, 30 days	85, photosynthesis
Poplar, yellow	43	588-880 (0.45)	9/day, 30 days	82, leaf drop; 0, height
Maple, silver	44	588 (0.30)	13 weeks 8/day, 5 days/week	50, leaf drop; 78, height
Ash, white	45	588 (0.30)	13 weeks 8/day, 5 days/week	66, leaf drop; 0, height
Sycamore	46	588 (0.30)	13 weeks 8/day, 5 days/week	0, leaf drop; 22, height
Maple, sugar	47	588 (0.30)	13 weeks 8/day, 5 days/week	28, leaf drop; 64, height
Corn, sweet, cultivar Golden Midget[c]	48	98 (0.05)	6/day, 64 days	9, kernel dry wt; 14, injury (12, avg. 4 yield responses)
Pine, ponderosa[c]	49	196 (0.10)	6/day, 64 days	45, 25, 35 for same responses
	50	196 (0.10)	6/day, 126 days	12, root length 21, stem dry wt; 26, root dry wt
Pine, western white[c]	51	196 (0.10)	6/day, 126 days	13, foilage dry wt 9, stem dry wt
Soybean, cultivar Dare[c]	52	98 (0.05)	6/day, 133 days	3, seed yield; 22, plant fresh wt; 19, injury, defoliation, no reduction in growth or yield
Poplar, hybrid	53	196 (0.10)	6/day, 133 days	55, 65, 37 for same responses
	54	290 (0.15)	8/day, 5 days/week 6 weeks	50, shoot dry wt; 56, leaf dry wt; ; 47, root dry wt

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[a] Modified from National Research Council (1977); cited in U.S. Environmental Protection Agency (1978).

[b] Numbers in this column are keyed to numbers in Fig. 6-6.

[c] Studies conducted under field conditions, except that plants were enclosed to ensure controlled pollutant doses. Plants grown under conditions making them more sensitive.

experiments conducted under more controlled conditions (greenhouses, indoor chambers, potted plants) are discussed primarily as they relate to the field studies.

6.4.3.2.1.1 Open-top chamber studies. Each of the studies described in this section used charcoal-filtered air as the lowest O_3 concentration (control). To create a range of concentrations, O_3 was added to either charcoal-filtered air or to air containing ambient levels of O_3. To summarize the data, yield loss was derived from the plant performance in charcoal-filtered air; this approach contrasts with the approach used in the NCLAN studies (e.g., Heck et al., 1982; Heck et al., 1983a) where yield loss was calculated from an assumed natural O_3 background level of 0.025 ppm. For this reason the yield loss values in this section may differ from those reported in various NCLAN studies even though the same exposure-response equations were used.

One of the major objectives of most of the studies cited in this section was to develop exposure-response functions relating plant changes in plant performance (yield) and O_3 exposure (concentration and duration). To derive the exposure-response functions, various linear and nonlinear curve-fitting approaches have been used. The initial NCLAN studies used either linear or plateau-linear functions to relate changes in plant yield to a 7-hr seasonal mean O_3 concentration (Heck et al., 1982). As discussed in greater detail in Section 6.4.3.3, however, the linear curve frequently introduced a bias into the data and should be used with caution. Subsequently, a Weibull function (Rawlings and Cure, 1985) was used to develop exposure-response functions for NCLAN data. The authors indicated that the Weibull was one of a series of curvilinear functions that could have been used but that the Weibull had a number of desirable properties and the curve fit the data well. The initial use of the Weibull with NCLAN data (Heck et al., 1983a) was based on treatment means for plant yield and O_3 concentration. The more recent publications of NCLAN data have used the individual chamber means for plant yield and O_3 exposure to derive the parameters of the Weibull function (e.g., Heck et al., 1984a,b; Kress and Miller, 1985a). The use of treatment means rather than plot means will alter variance estimates associated with the parameters as well as the parameters themselves. To determine possible differences between the two different methods of calculating the Weibull parameters, the concentrations that would be predicted to cause a 10 percent yield loss were compared for the same data set using both methods for several crops or cultivars. The difference between 7-hr seasonal mean O_3 concentrations predicted to cause

10 percent yield loss, using plot and treatment means, ranged between 0.053 ppm less to 0.011 ppm greater, with several values showing no difference between the methods.

To estimate the impact of O_3 on yield at a common O_3 concentration for all the studies, the derived equations were used to estimate the yield loss at a particular exposure condition rather than from the individual means. Graphs of the exposure response equations and the data used to derive them are presented to show the goodness of fit of the Weibull function to the data. The data are grouped into legume, grain, fiber, and horticultural crops. The parameters of the Weibull curves relating plant yield to the 7-hr seasonal mean O_3 concentration are listed in Table 6-19. The parameters for the Weibull equations can be used to calculate the regression equation. The O_3 concentration in charcoal-filtered air was used to calculate percentage yield loss. The table also contains the calculated 7-hr seasonal mean concentrations that are predicted to cause 10 and 30 percent yield reductions. The values were selected to provide an indication of crop or cultivar sensitivity.

The impact of O_3 on soybean yield has been investigated using nine cultivars grown at four different locations (Table 6-19, Figure 6-12). Each location grew different cultivars and usually for only 1 year in developing the exposure-response functions. The 7-hr seasonal mean O_3 concentration that was predicted to induce a 10 percent yield loss ranged from a low of 0.032 ppm for Hodgson to a high of 0.076 ppm for Forrest, with a mean for the nine cultivars of 0.048 ppm. Two soybean cultivars, Davis and Williams, were studied for 2 successive years at the same location, permitting an estimation of year-to-year variability in the impact of O_3 on yield (Figure 6-13). At Raleigh, NC, a 7-hr seasonal mean concentration of 0.06 ppm was predicted to cause yield losses in the cultivar Davis of 23.1 and 16.5 percent for the years 1981 and 1982, respectively. At Beltsville, MD, the predicted yield loss for the cultivar Williams varied between 18.1 (1981) and 16.5 (1982) at a 7-hr seasonal mean concentration of 0.06 ppm. The year-to-year difference in predicted yield loss at the same concentration probably reflects differences in the environmental conditions.

Aside from soybean, only two other legume crops, kidney bean and peanut, have been studied (Table 6-19, Figure 6-14). Using the Weibull function, the yield of peanut would be predicted to be reduced 10 percent at a 7-hr seasonal

TABLE 6-19. ESTIMATES OF THE PARAMETERS FOR FITTING THE WEIBULL MODEL USING THE 7-HR SEASONAL MEAN OZONE CONCENTRATIONS[a,b]

Crop	Parameters for Weibull Model				Concentration for predicted yield losses of:	
	$\hat{\alpha}$	$\hat{\sigma}$	$\hat{c}$	CF[c]	10%[d]	30%[d]
LEGUME CROPS						
Soybean, Corsoy	2785.00	0.133	1.952	0.022	0.048	0.082
Soybean, Davis (81)	5593.00	0.128	0.872	0.025	0.038	0.071
Soybean, Davis (CA-82)[e]	4931.00	0.128	2.144	0.019	0.048	0.081
Soybean, Davis (PA-82)[e]	4805.00	0.103	4.077	0.019	0.059	0.081
Soybean, Essex (81)	4562.00	0.187	1.543	0.014	0.048	0.099
Soybean, Forrest (82-I)	4333.00	0.171	2.752	0.017	0.076	0.118
Soybean, Williams (81)	4992.00	0.211	1.100	0.014	0.039	0.093
Soybean, Williams (82-I)	5884.00	0.162	1.577	0.017	0.045	0.088
Soybean, Hodgson	2590.00	0.138	1.000	0.017	0.032	0.066
Bean, Kidney (FP)[f]	2878.00	0.120	1.171	0.019	0.033	0.063
Peanut, NC-6	7485.00	0.111	2.249	0.025	0.046	0.073
GRAIN CROPS						
Wheat, Abe (82)	5363.00	0.143	2.423	0.023	0.059	0.095
Wheat, Arthur 71 (82)	4684.00	0.148	2.154	0.023	0.056	0.094
Wheat, Roland	5479.00	0.113	1.633	0.023	0.039	0.067
Wheat, Vona	7857.00	0.053	1.000	0.022	0.028	0.041
Wheat, Blueboy II (T)	5.88	0.175	3.220	0.030	0.088	0.127
Wheat, Coker 47-27 (T)	5.19	0.171	2.060	0.030	0.064	0.107
Wheat, Holly (T)	4.95	0.156	4.950	0.030	0.099	0.127
Wheat, Oasis (T)	4.48	0.186	3.200	0.030	0.093	0.135
Corn, PAG 397	13968.00	0.160	4.280	0.015	0.095	0.126
Corn, Pioneer 3780	12533.00	0.155	3.091	0.015	0.075	0.111
Corn, Coker 16 (T)	240.00	0.221	4.460	0.020	0.133	0.175
Sorghum, DeKalb-28	8137.00	0.296	2.217	0.016	0.108	0.186
Barley, Poco	1.99	0.205	4.278	0.020	0.121	0.161
FIBER CROPS						
Cotton, Acala SJ-2 (81-I)	5546.00	0.199	1.228	0.018	0.044	0.096
Cotton, Acala SJ-2 (82-I)	5872.00	0.088	2.100	0.012	0.032	0.055
Cotton, Stoneville	3686.00	0.112	2.577	0.026	0.047	0.075
HORTICULTURAL CROPS						
Tomato, Murrieta (81)	32.90	0.142	3.807	0.012	0.079	0.108
Tomato, Murrieta (82)	32.30	0.082	3.050	0.012	0.040	0.059
Lettuce, Empire (T)	1245.00	0.098	1.220	0.043	0.053	0.075
Spinach, America (T)	21.20	0.142	1.650	0.024	0.046	0.082
Spinach, Hybrid (T)	36.60	0.139	2.680	0.024	0.043	0.082
Spinach, Viroflay (T)	41.10	0.129	1.990	0.024	0.048	0.080

TABLE 6-19 (cont'd). ESTIMATES OF THE PARAMETERS FOR FITTING THE USING THE 7-HR SEASONAL MEAN OZONE CONCENTRATIONS[a,b]

	Parameters for Weibull Model				Concentration for predicted yield losses of:	
Crop	$\hat{\alpha}$	$\hat{\sigma}$	$\hat{c}$	CF[c]	10%[d]	30%[d]
Spinach, Winter Bloom (T)	20.80	0.127	2.070	0.024	0.049	0.080
Turnip, Just Right (T)	10.89	0.090	3.050	0.014	0.043	0.064
Turnip, Pur Top W.G. (T)	6.22	0.095	2.510	0.014	0.040	0.064
Turnip, Shogoin (T)	4.68	0.096	2.120	0.014	0.036	0.060
Turnip, Tokyo Cross (T)	15.25	0.094	3.940	0.014	0.053	0.072

[a] Data are from Heck et al. (1984b) and are based on individual plot means unless the crop name is followed by "(T)". The "T" indicates that the parameters were based on treatment means and the data are from Heck et al. (1983a). The parameters given in Heck et al. (1983a, 1984b) also contain the standard errors of the parameters.

[b] All estimates of $\hat{\sigma}$ are in ppm. The yield is expressed as kg/Ha for all crops except barley--seed weight (g per head); tomato (both years)--fresh weight (kg per plot); cotton--lint + seed weight (kg/Ha); peanut--pod weight (kg/Ha). In cases where the estimated $\hat{c}$ parameter is exactly 1.0, it has been bounded from below to obtain convergence in the nonlinear model fitting routine. Parameters were estimated from data not showing the expected Weibull form. Caution should be used in interpreting these Weibull models. Other models might better describe the behavior observed in these experiments. For those crops whose name is followed by "(T)" the yield is expressed as g/plant.

[c] The O_3 concentration in the charcoal filtered chambers expressed as a 7-hr seasonal mean concentration.

[d] The 7-hr seasonal mean O_3 concentration (ppm) that was predicted to cause a 10 or 30 percent yield loss (compared to charcoal-filtered air).

[e] CA and PA refer to constant and proportional O_3 addition.

[f] Only the bean data from the full plots are shown. The partial plot data are given in Heck et al. (1984b).

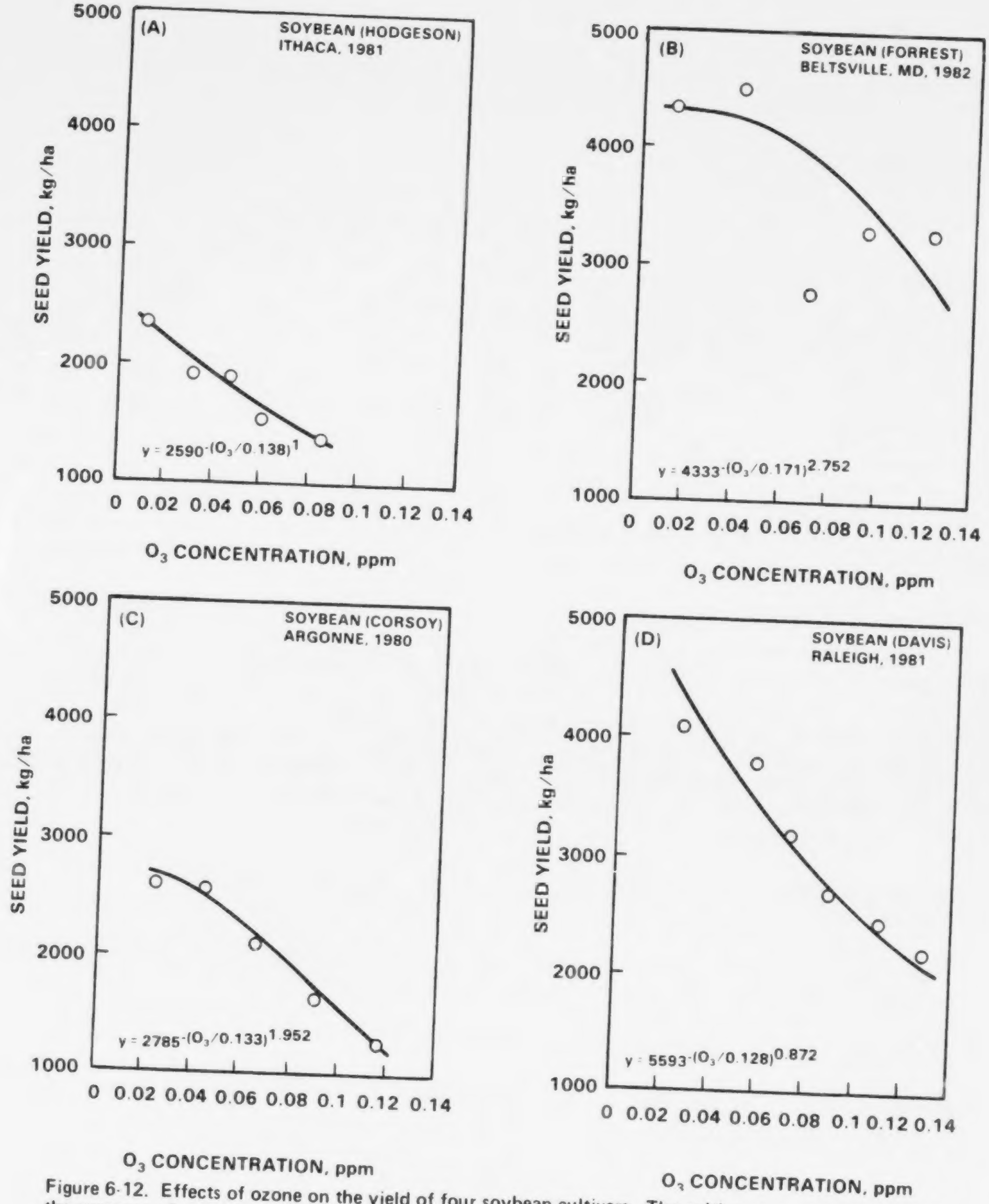

Figure 6-12. Effects of ozone on the yield of four soybean cultivars. The cultivars were selected to show the response of one cultivar at each of the four locations where studies were conducted. The O_3 concentrations are expressed as the 7-hr seasonal means. (A) Each point represents the mean of two undisturbed full plots. The regression equation was based on individual chamber ozone and yield values. The Weibull curve is from Heck et al. (1984b). Note that c = 1.0 and the model was forced to converge. This means that "parameters were estimated from data not showing the expected Weibull form" (Heck et al. 1984b). Another curve for g/plant is in Heck et al. (1982). (B) The regression equation was based on individual chamber ozone and yield values. The Weibull curve is from Heck et al. (1984b). (C) The O_3 monitoring period for the seasonal mean is 9 days shorter than the O_3 exposure period. Each point represents the mean of four chambers. The data are from Kress and Miller (1983). Yields expressed in g/plant can also be found in Heck et al. (1983) and Heck et al. (1982). The regression was based on yield and ozone values for individual chambers. The Weibull equation is from Heck et al. (1984b). Another curve for yield in g/plant is in Heck et al. (1983). (D) Each point represents the mean of two chambers. Data in g/meter of row can be found in Heagle et al. (1983) and in Heck et al. (1982). To convert from g/m^3 to kg/ha, multiply by 10.1. The regression was based on yield and ozone values for individual chambers. The Weibull equation is from Heck et al. (1984b). Another Weibull curve for g/plant is given in Heck et al. (1983).

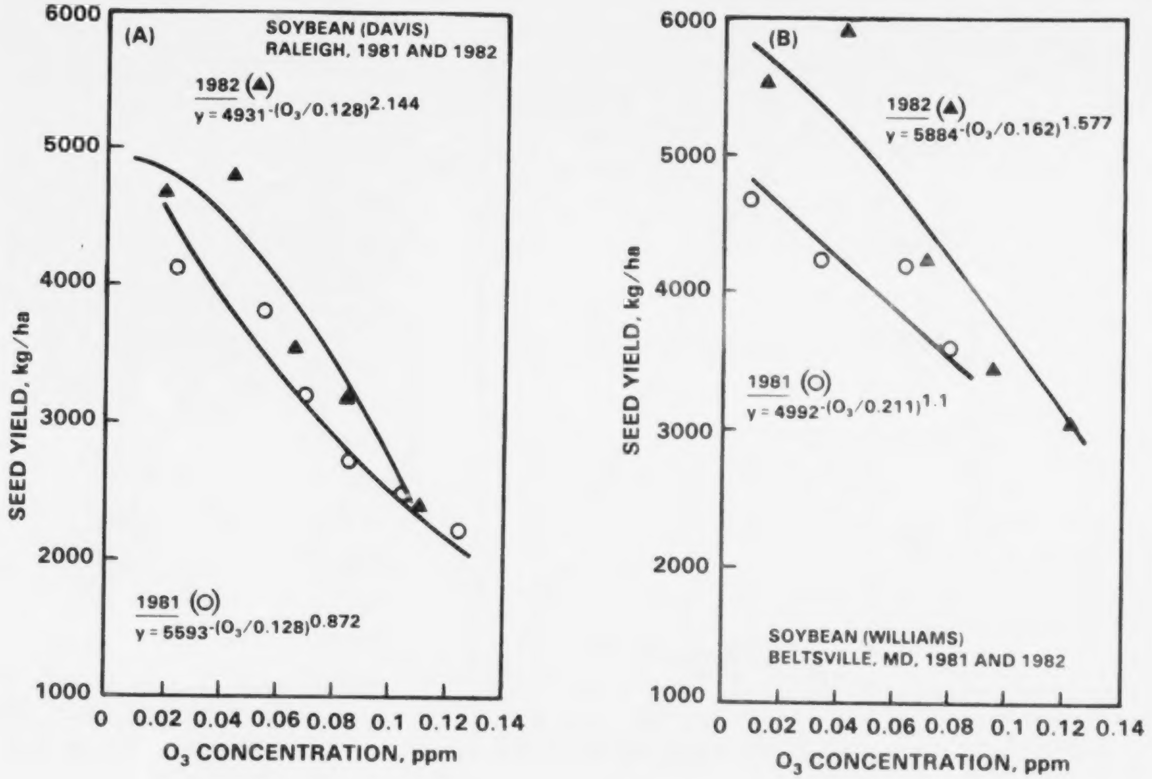

Figure 6-13. Comparison of the effects of ozone on soybean yields on the same cultivars exposed for successive years at two locations. The O_3 concentrations are expressed as the 7-hr seasonal means. (A) The data for Davis (1981) are described in the caption to Figure 6-12. For Davis (1982), each yield value is the mean of two chambers. The Weibull equations are from Heck et al. (1984b). (B) In 1981 the points at 0.01 and 0.035 ppm O_3 were the means of three chambers. The other points shown are values for one chamber only. These data are taken from a factorial experiment with six SO_2 and four O_3 levels. Only the control SO_2 level is shown here. The regression was based on yield and ozone values for individual chambers. The Weibull curves are from Heck et al. (1984b). Other curves for g/plant are given in Heck et al. (1983a). In 1982, the data came from a factorial experiment with three SO_2, five O_3, and two moisture levels. Only the control SO_2 and moisture levels were used in the figure. The regression equations were based on individual chamber ozone and yield values. The Weibull curve is from Heck et al. (1984b).

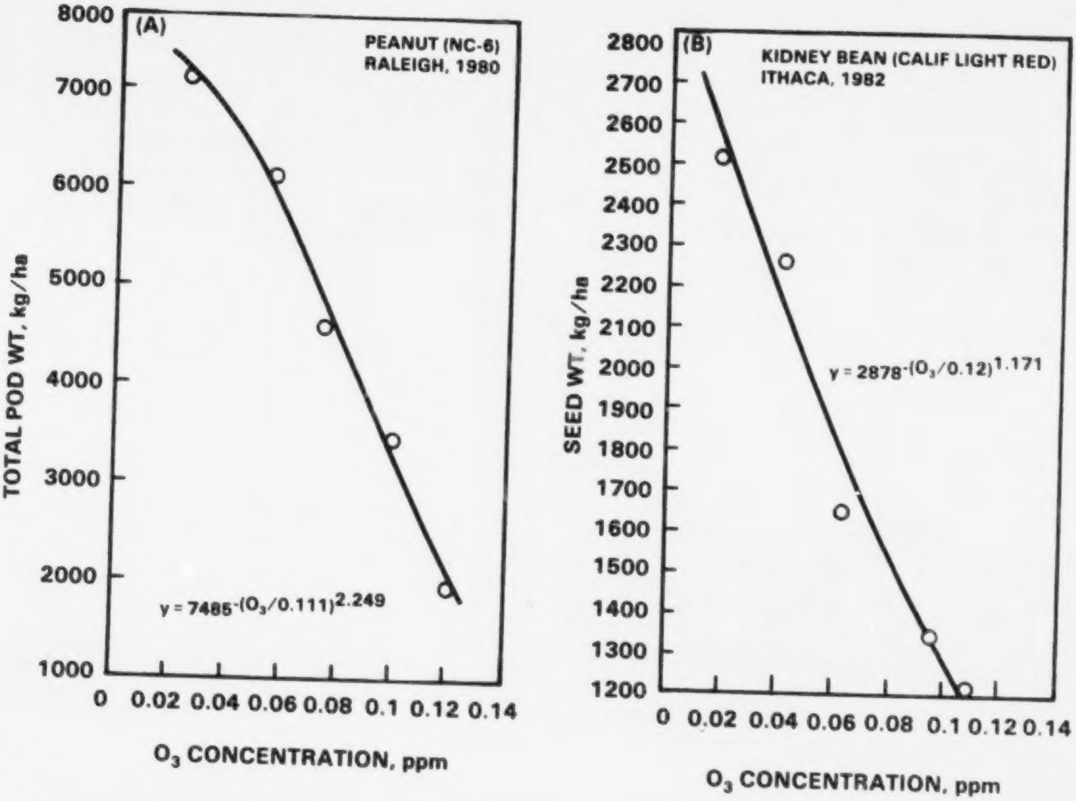

Figure 6-14. Effects of ozone on the yield of peanut and kidney bean. The O_3 concentrations are expressed as the 7-hr seasonal means. (A) Each point represents the mean of four chambers. Yields were multiplied by 50.5 to convert from g/plant to kg/ha. The regression was based on yield and ozone values for individual chambers. The Weibull equation is from Heck et al. (1984b). (B) Each point represents the mean of two undisturbed full plots. The regression was based on individual chamber values for yield and ozone. The Weibull equation is from Heck et al. (1984b).

mean concentration of 0.046, which was similar to the mean response of the 9 soybean cultivars. Kidney bean appears to be similar in O_3 sensitivity to peanut or most of the soybean cultivars. Kidney bean yield was predicted to be reduced 10 percent at a 7-hr seasonal mean concentration of 0.033. When the data were analyzed using linear regression analysis (Kohut and Laurence, 1983) a 7 percent reduction in yield was predicted to occur at a 7-hr seasonal mean concentration of 0.06 ppm.

Winter wheat yield appeared to be relatively less sensitive to O_3 than the legumes based on the yield reductions of four cultivars (Table 6-20). The yield of all four cultivars was significantly reduced (11 to 25 percent) at 0.10 ppm (7-hr seasonal mean), but only one cultivar was significantly affected (11 percent) at 0.06 ppm (Heagle et al., 1979c). These data have subsequently been re-evaluated using quadratic (Heagle and Heck, 1980), linear (Heck et al., 1982), and Weibull functions (Heck et al., 1983a). Based on visual inspection of the data, it appears that the curvilinear models fit the data better than the linear one. In addition to these four cultivars, which were studied at Raleigh, NC, one wheat cultivar was studied at Ithaca, NY (for 1 year) and three cultivars were studied at Argonne, IL (two cultivars for 2 years). Examples of the relationship between wheat yield and O_3 concentrations are shown for cultivars at three different locations (Figure 6-15). The 7-hr seasonal mean O_3 concentration that was predicted to induce a 10 percent yield loss ranged from a low of 0.028 ppm for Vona (Ithaca) to a high of 0.099 ppm for Holly (Raleigh), with a mean for the eight cultivars of 0.068 ppm. The winter wheat cultivars displayed a greater range in the 7-hr seasonal means predicted to cause 10 and 30 percent yield reductions than did the soybean cultivars. Using the 7-hr seasonal mean predicted to cause a 10 percent yield reduction, wheat cultivars such as Vona and Roland (Argonne) appeared to be similar in sensitivity to soybean. The other wheat cultivars appeared to be relatively tolerant of O_3. Two wheat cultivars, Abe and Arthur-71, were studied for 2 successive years at Argonne, IL (Kress et al., 1985, Figure 6-16), permitting an estimation of year-to-year variability in the effect of O_3 on yield. For Abe, a 7-hr seasonal mean concentration of 0.06 ppm was predicted to cause yield losses of 10 and 0 percent for the years 1982 and 1983, respectively. The predicted yield loss for the cultivar Arthur-71 varied between 8.8 (1982) and 3.2 (1983) percent at a 7-hr seasonal mean concentration of 0.06 ppm. For the cultivar Abe, the shape of the regression equation varied between years, but for Arthur-71 it was similar between

TABLE 6-20. EFFECTS OF OZONE ADDED TO AMBIENT AIR IN OPEN-TOP CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control	Monitoring method[b]	Calibration method[c]	Reference
Field corn (Coker 16)	0.02	Beginning 25 days after planting for 88 days, Seasonal 7-hr average (0830-1530 ST)	Control	Chem.	1% NBKI	Heagle et al. (1979a)
	0.07		+3, seed wt/plant; +2, wt/seed			
	0.11		4, seed wt/plant; 1, wt/seed			
	0.15		16[d], seed wt/plant; 9[d], wt/seed			
Field corn (Coker 16)	0.02	Beginning 25 days after planting for 88 days, Seasonal 7-hr average (0830-1530 ST)	Control	Chem.	1% NBKI	Heagle et al. (1979a)
	0.15		12[d], seed wt/plant; 15[d], wt/seed			
(FR632 X FR619)	0.02		Control			
	0.15		37[d], seed wt/plant; 25[d], wt/seed			
(H95 X FR64A)	0.02		Control			
	0.15		40[d], seed wt/plant; 30[d], wt/seed			
Winter wheat (soft red) (Blueboy II)	0.03	Beginning when plants were 28 to 45 cm tall for 53 days Seasonal 7-hr average (0930-1530 ST)	Control	Chem.	1% NBKI	Heagle et al. (1979c)
	0.06		2, seed wt/plant			
	0.10		15[d], seed wt/plant			
	0.13		31[d], seed wt/plant			
(Coker 47-27)	0.03		Control			
	0.06		11[d], seed wt/plant			
	0.10		25[d], seed wt/plant			
	0.13		43[d], seed wt/plant			
(Holly)	0.03		Control			
	0.06		1, seed wt/plant			
	0.10		11[d], seed wt/plant			
	0.13		33[d], seed wt/plant			
(Oasis)	0.03		Control			
	0.06		1, seed wt/plant			
	0.10		11[d], seed wt/plant			
	0.13		26[d], seed wt/plant			

TABLE 6-20 (cont'd). EFFECTS OF OZONE ADDED TO AMBIENT AIR IN OPEN-TOP CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control	Monitoring method[b]	Calibration method[c]	Reference
Spinach (America)	0.024	Beginning 10 days after planting for 38 days, Seasonal 7-hr average (0820-1520 ST)	Control	Chem.	1% NBKI	Heagle et al. (1979b)
	0.056		23, fresh wt of shoots			
	0.096		39[d], fresh wt of shoots			
	0.129		70[d], fresh wt of shoots			
(Winter Bloomsdale)	0.024		Control			
	0.056		19, fresh wt of shoots			
	0.096		44[d], fresh wt of shoots			
	0.129		73[d], fresh wt of shoots			
(Hybrid 7)	0.024		Control			
	0.056		4, fresh wt of shoots			
	0.096		35[d], fresh wt of shoots			
	0.129		61[d], fresh wt of shoots			
(Viroflay)	0.024		Control			
	0.056		26, fresh wt of shoots			
	0.096		35[d], fresh wt of shoots			
	0.129		72[d], fresh wt of shoots			

[a] Where a column entry is blank the information is the same as above.

[b] Chem = chemiluminescence.

[c] 1% NBKI = 1% neutral buffered potassium iodide.

[d] Significant effect at $p = 0.05$.

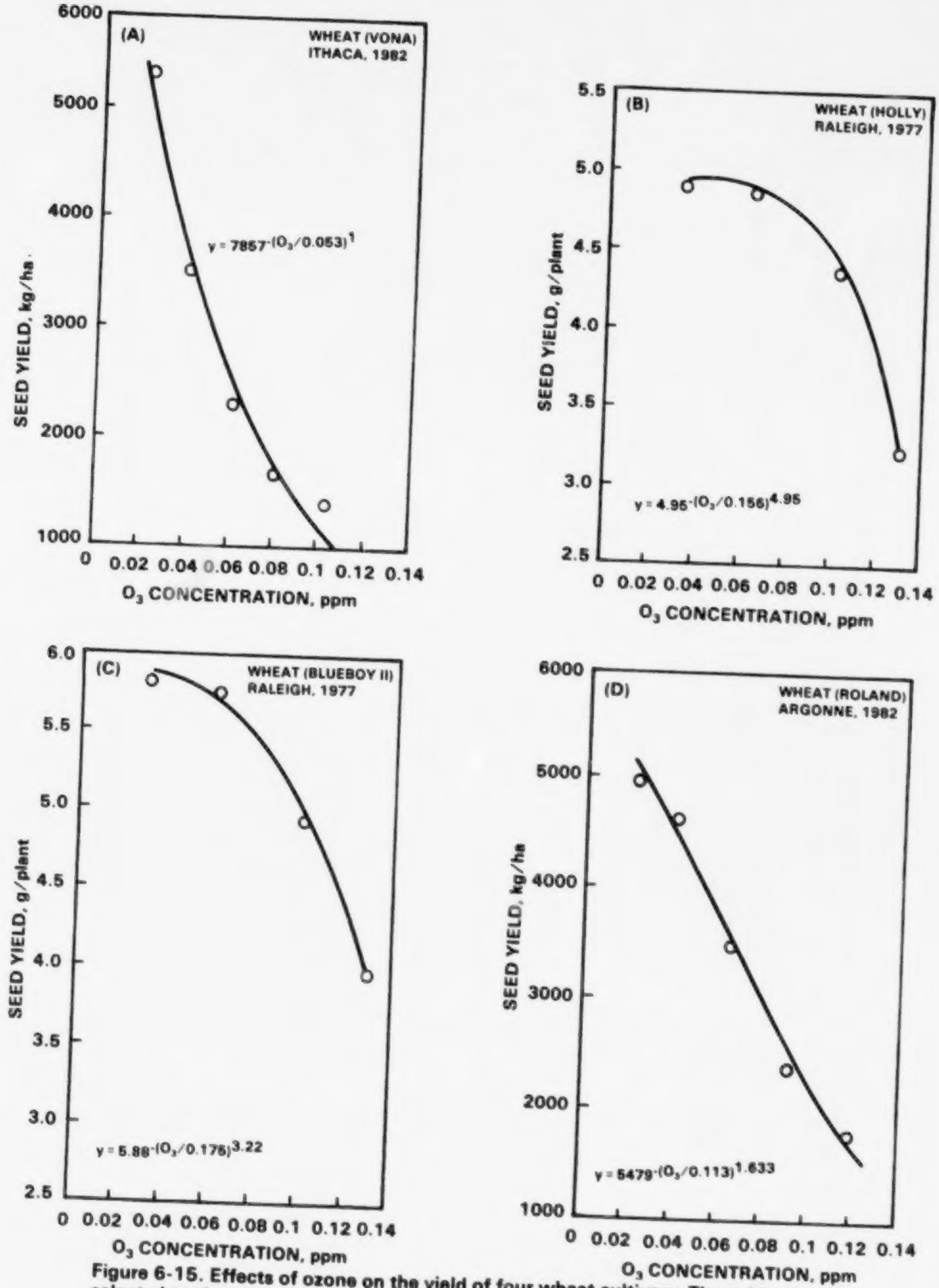

Figure 6-15. Effects of ozone on the yield of four wheat cultivars. The cultivars were selected to show the response at several locations. The O_3 concentrations are expressed as the 7-hr seasonal means. (A) Each point represents the mean of four chambers. The regressions were based on individual chamber ozone and yield values. The Weibull equation is from Heck et al. (1984b). Note that c = 1.0 and the model was forced to converge. "The parameters were estimated from data not showing the expected Weibull form" (Heck et al., 1984b). (B-C) Each point represents the mean of four chambers. Data are from Heagle et al. (1979c). The regressions were based on mean O_3 concentrations for each treatment and individual chamber yields. The Weibull equations are from Heck et al. (1983). Note that the yields for these figures are in different units from A through D. (D) Each point represents a mean of four chambers adjusted for number of heads per meter by analysis of covariance. The data are from Kress et al. (1985) and Heck et al. (1983). The regressions were based on individual chamber ozone and yield values. The Weibull equations are from Kress et al. (1985); other equations can be found in Heck et al. (1984).

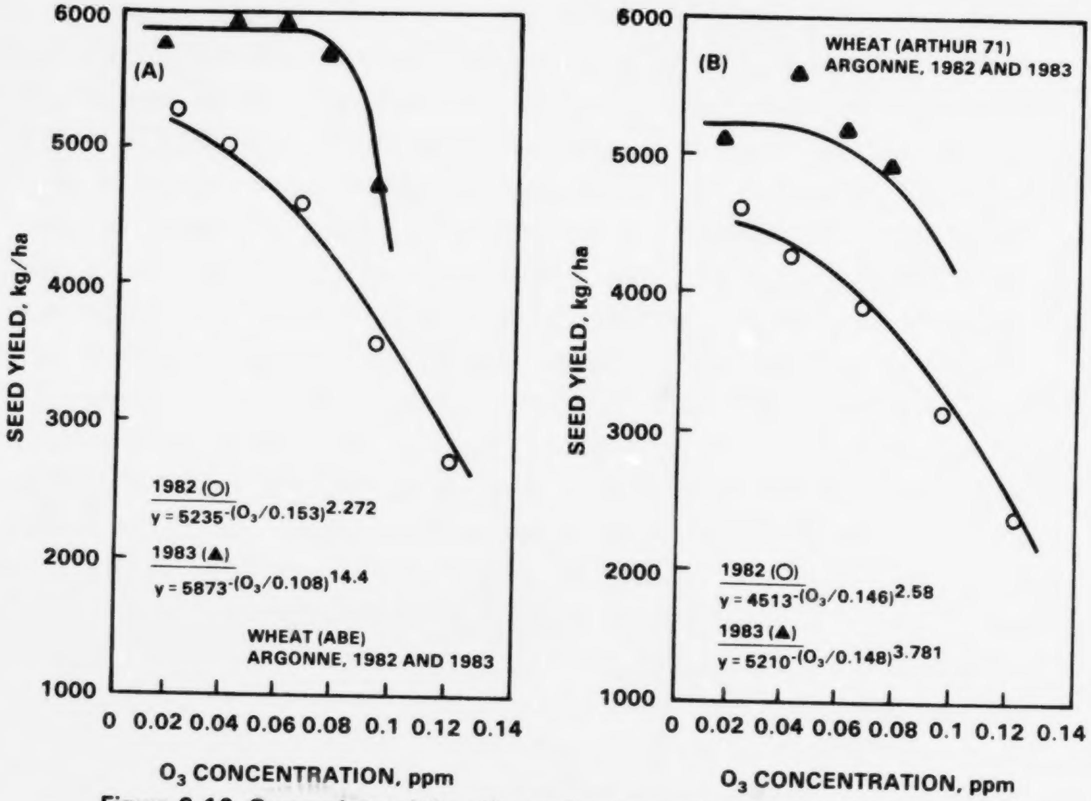

Figure 6-16. Comparison of the effects of ozone on yields of the same wheat cultivars exposed for successive years at Argonne, IL. The O_3 concentrations are expressed as the 7-hr seasonal means. For 1982 each point on the graph represents the mean of four chambers, and for 1983 each point represents the mean of three chambers. In both years the means were adjusted to a common number of heads per meter by analysis of covariance. The data are from Kress et al. (1985). The regressions were based on individual chamber ozone and yield values. The Weibull equations are from Kress et al. (1985). For 1983 the alpha estimate has been corrected to 5210 *(personal communication from L.W. Kress, Argonne National Laboratory, to D.T. Tingey, U.S. EPA, 1985).* Other Weibull equations for the 1982 data are found in Heck et al. (1984b).

years, probably contributing to lower year-to-year variability. The year-to-year difference in predicted yield loss at the same concentration probably reflects the influence of differences in the environmental conditions on plant response to O_3.

The effects of O_3 on field corn have received less study than winter wheat. The impact of O_3 on the yield of field corn was initially studied with Coker 16; the results of this study have been analyzed by several different methods and published in several different forms. The data were initially presented in tabular form using mean comparison tests (Heagle et al., 1979a; Table 6-20) and subsequently analyzed using quadratic (Heagle and Heck, 1980) and linear (Heck et al., 1982) regression models. Reductions in seed yield (g/plant) were originally shown to be 4 percent at a 7-hr seasonal mean concentration of 0.11 ppm and 16 percent at 0.15 ppm O_3 when compared to a 0.020 ppm control (Table 6-20). The quadratic regression predicted a yield increase of 1 percent at 0.06 ppm and a yield reduction of 3 percent at a 7-hr seasonal mean concentration of 0.10 ppm. The linear equation showed significant lack of fit to the data; therefore it was not considered. Using the Weibull parameters for Coker 16 (Table 6-19, Figure 6-17), a 10 percent yield loss was predicted to occur at a 7-hr seasonal mean concentration of 0.133 ppm. The impact of ozone on two midwestern corn cultivars has also been studied (Table 6-19); these cultivars appeared to be more sensitive to O_3 than Coker 16. Using the Weibull parameters, yield reductions of 10 percent were predicted to occur at 7-hr seasonal mean concentrations of 0.075 and 0.095 ppm for Pioneer 3780 and PAG 397, respectively. Kress and Miller (1985b) subsequently analyzed the data for Pioneer 3780 (Figure 6-17B) and PAG 397 using Weibull, quadratic, and plateau-linear models and found no statistical difference among them.

Sorghum (Figure 6-17C) was approximately as sensitive to O_3 as field corn (Table 6-19); the Weibull function predicted a 10 percent yield loss at a 7-hr seasonal mean concentration of 0.108 ppm. Quadratic, Weibull, and plateau-linear models all adequately described the response of grain sorghum to O_3 (Kress and Miller, 1985a).

Poco barley (Figure 6-17D) (Poco) was as tolerant of O_3 as the more tolerant corn cultivar (Coker 16); using the Weibull function, a 10 percent yield loss was predicted to occur at a 7-hr seasonal mean O_3 concentration of 0.121 ppm (Table 6-19). Temple et al. (1985b) subsequently showed that the

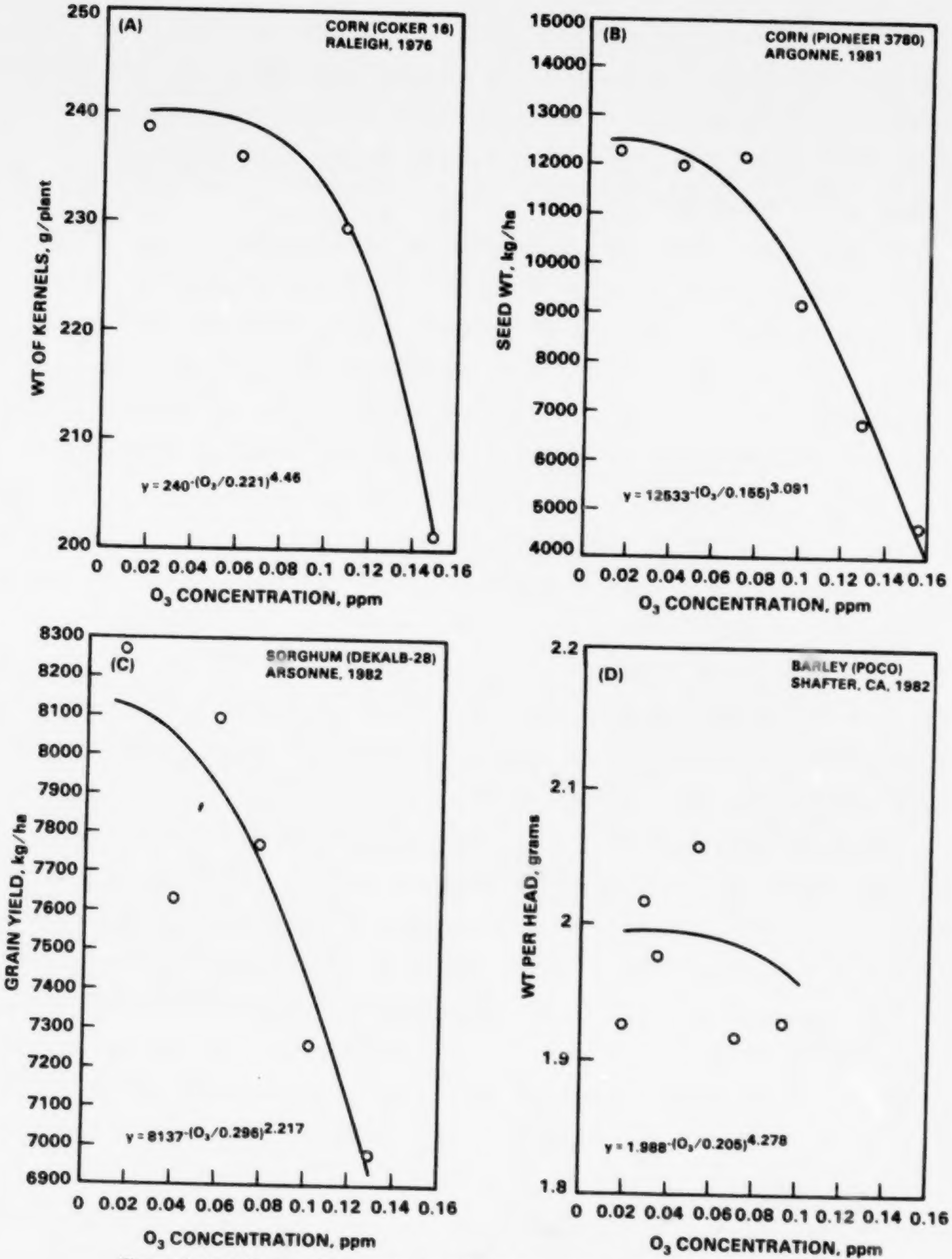

Figure 6-17. Effects of ozone on the yield of corn (two cultivars), sorghum and barley. The O_3 concentrations are expressed as the 7-hr seasonal means. (A) Each point represents the mean of five chambers. The regression equation was based on individual chamber yield values and ozone treatment means. Data are from Heagle et al. (1979a). The Weibull equation is from Heck et al. (1983a). (B) Each point represents the mean of three chambers; data are from Kress and Miller (1985b). The Weibull equation is from Heck et al. (1984b) and the regression was done on individual chamber values for yield and ozone concentration. Another set of curves can be found in Kress and Miller (1985b), and a set of curves for yield in g/plant are in Heck et al. (1983a). (C) Each point represents the mean of three chambers. The regression was based on yield and ozone values for individual chambers. The data can be found in Kress and Miller (1985a), and the Weibull equation is from Heck et al. (1984b). Another curve can be found in Kress and Miller (1985a). (D) Each yield value represents the mean of four chambers. The regression was based on yield and ozone values for individual chambers. The Weibull equation is from Heck et al. (1984b).

yield of two barley cultivars was not reduced by ambient O_3 in the Central Valley of California. Even at twice ambient concentrations the yield was not affected. The twice-ambient concentration 0.094 (7-hr seasonal mean) was substantially lower than the concentration (0.121 ppm) predicted by the Weibull to reduce yield by 10 percent.

A 2-year field study was conducted in the Central Valley of California to determine the impact of O_3 on the yield of cotton. Using the Weibull parameters (Table 6-19, Figure 6-18A), a 10 percent yield reduction was predicted to occur at 7-hr seasonal mean O_3 concentrations of 0.044 and 0.032 ppm in 1981 and 1982, respectively. Based on these data it appears that cotton is approximately as sensitive to O_3 as soybean or peanut. Based on the Weibull function for Acala SJ-2 cotton, a 7-hr seasonal mean concentration of 0.06 ppm was predicted to cause yield losses of 16.2 and 35.1 percent for the years 1981 and 1982, respectively. Using other exposure-response functions published by Temple et al. (1985a), the year-to-year variation in yield loss was 18 and 27 percent for the years 1981 and 1982, respectively. The cotton data set illustrates two different types of variation that may occur. Differences in yield loss vary between years at the same 7-hr seasonal mean O_3 concentration. The authors (Temple et al., 1985a) showed that there were significant climatic differences between the two years that contributed to the variation. Also, the study shows that different exposure-response functions may also yield different predicted yield loss estimates. For cotton grown in the Southeastern U.S. (Raleigh, NC) a 10 percent yield reduction was predicted to occur at a 7-hr seasonal mean of 0.047 ppm (Figure 6-18B). Based on these data it appears that cotton is approximately as sensitive to O_3 as soybean or peanut.

The yield of tomato also showed large year-to-year variation in sensitivity to O_3 (Table 6-19, Figure 6-19A). Based on the Weibull parameters, a 10 percent reduction in yield was predicted to occur at 7-hr seasonal mean O_3 concentrations of 0.079 and 0.040 ppm in 1981 and 1982, respectively. The yield of lettuce was predicted to be reduced 10 percent at a seasonal mean concentration of 0.053 ppm (Table 6-19, Figure 6-19B).

The effects of O_3 on the yield (weight) of four spinach cultivars have been studied (Table 6-20). All four cultivars exhibited significant yield reductions (35 to 44 percent) when exposed to 0.096 ppm O_3 (7-hr seasonal mean), compared to a control of 0.024 ppm (Heagle et al., 1979b). Nonsignificant yield reductions of 4 to 26 percent were noted at 0.056 ppm O_3. All the

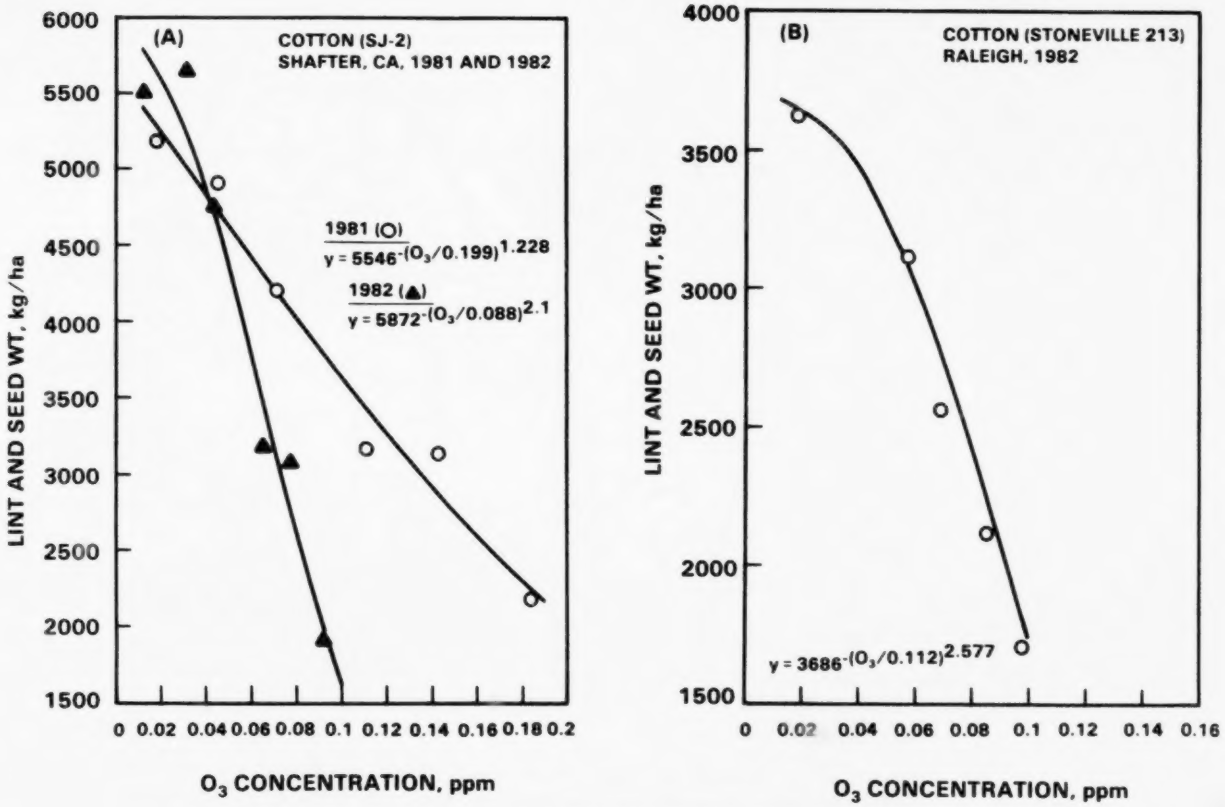

Figure 6-18. Effects of ozone on the yield of two cotton cultivars grown at two locations. The O_3 concentrations are expressed as 7-hr seasonal means. (A) Each point represents the mean of two chambers. There were six O_3 levels and two irrigation levels in this experiment. Only chambers with normal irrigation were included in this figure. The regression was based on yield and ozone values for individual chambers. The Weibull equation is from Heck et al. (1984b). In 1982, the monitoring period used to calculate the 7-hr seasonal mean was 41 days longer than the period that O_3 was added experimentally to the chambers. (B) Each point represents the mean of two chambers. The regression was based on individual chamber values for yields and ozone. The Weibull equation is from Heck et al. (1984b).

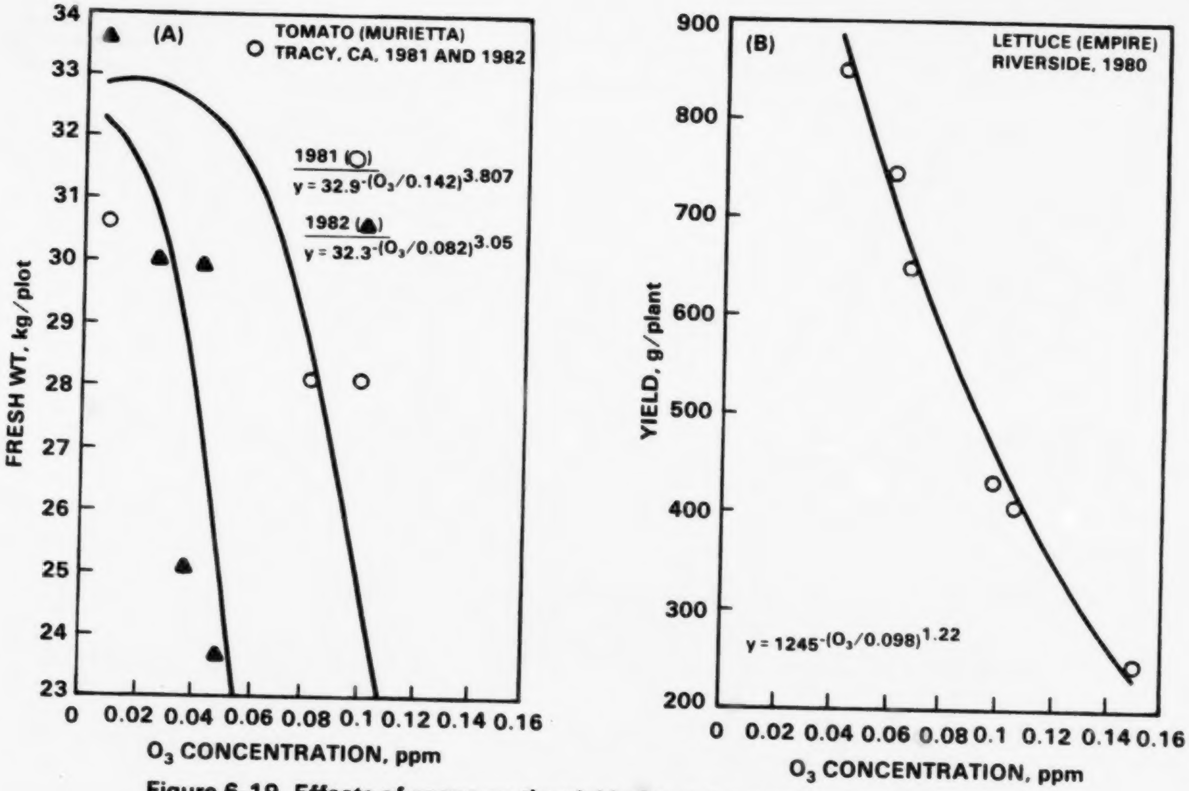

Figure 6-19. Effects of ozone on the yield of tomatoes and lettuce. The O_3 concentrations are expressed as the 7-hr seasonal means. (A) The yields at 0.012 (1981) and 0.011 ppm (1982) were the means of two chambers; all other yield values were from one chamber only. The regression was based on individual chamber yield and ozone values. The Weibull curve is from Heck et al. (1984b). (B) Each point represents the mean of four chambers. Data are from Heck et al. (1982). The regression is based on mean O_3 concentrations for each treatment and individual yield values for each chamber. The Weibull equation is from Heck et al. (1983a).

cultivars, except Viroflay, displayed some foliar injury that could impair its intended use even though the weight of the plants was not reduced. The same data were subjected to reanalysis using linear (Heck et al., 1982) and Weibull (Heck et al., 1982, Figure 6-20A,B) functions. Using the Weibull parameters, a 10 percent reduction in yield was predicted to occur at 7-hr seasonal mean concentrations of 0.043 to 0.049 ppm. This range in predicted concentrations is smaller than that observed in other crops such as soybean or wheat.

The effects of O_3 on the yield (weight) of four turnip cultivars has been studied. One cultivar, Tokyo Cross, was studied during 2 years (Heck et al., 1982; Heagle et al., 1985, Figure 6-20C,D). The data were analyzed with four models, linear, quadratic, plateau-linear, and Weibull; and statistical tests for lack of fit were performed. The plateau-linear model showed significant lack of fit with one cultivar and the other three showed significant lack of fit with two cultivars each. Based on the Weibull parameters, the 7-hr seasonal mean O_3 concentration that would be predicted to cause a 10 percent yield reduction ranged from a low of 0.036 (Shogoin) to a high of 0.053 ppm (Tokyo Cross). Part of the yield loss was attributed to an acute injury episode from a low concentration of O_3 after a period of dark, cool, rainy weather (Heagle et al., 1985). These data illustrate one of the problems with the 7-hr seasonal mean concentration as a statistic for adequately characterizing O_3 exposure and the resultant effects. The cultivar Tokyo Cross was grown 2 years, permitting an illustration of year-to-year variation in the predicted yield response. Based on the Weibull function, a seasonal mean concentration of 0.06 ppm was predicted to cause yield reductions of 27.2 and 15.6 percent for the years 1979 and 1980, respectively.

6.4.3.2.1.2. Use of chemical protectants to estimate yield loss. Chemical protectants have several advantages for estimating yield loss. The crops are not grown in chambers but are grown under field conditions using standard cultural practices; and are exposed to ambient environmental conditions. It is also possible to have several replications in a field and to have a number of fields included in the study area, and the plants are exposed to the temporal variations in pollutant concentrations occurring at the location(s). With chemical protectants, however, only a single pollutant treatment is possible at a location and this prevents the development of exposure-response functions as can be done with exposure chambers. When chemical protectants are used to estimate yield loss, care must be exercised in interpreting the data because

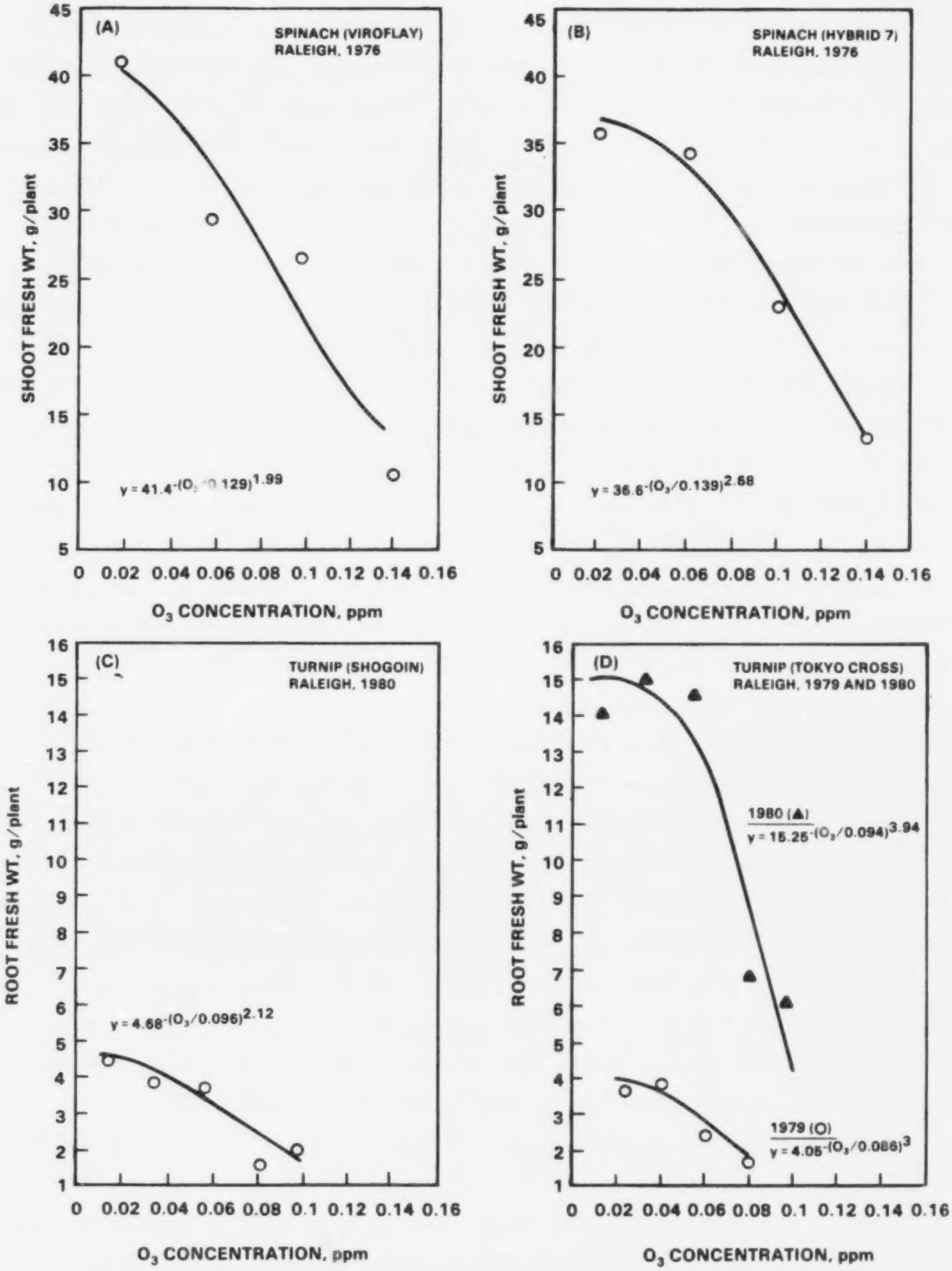

Figure 6-20. Effects of ozone on the yield of spinach and turnip cultivars. The O_3 concentrations are expressed as 7-hr seasonal means. (A-B) Each point represents the mean of three chambers. Data are from Heagle et al. (1979b). The regressions were based on mean O_3 concentrations for each treatment and individual yield values for each chamber. The Weibull equations are from Heck et al. (1983a). (C-D) Each point represents the mean of four chambers except for Tokyo Cross, 1979, which represents the mean of two chambers. The regressions were based on mean O_3 concentrations for each treatment and individual yield values for each chamber. The data and the Weibull equations are from Heagle et al. (1985). The same data can be found in Heck et al. (1982).

the chemical protectant, in the absence of the pollutant, may alter plant growth. In addition, the chemical protectant may not be effective against all the phytotoxic chemicals that may be present in the environment, with the consequence that the resultant yield loss would be underestimated. An underestimation would also occur if the protectant chemical did not prevent all the impacts of the pollutant at all ambient concentrations. Even with these limitations, however, researchers have concluded that antioxidant chemical protectants provide a readily available objective method for assessing the effects of ozone on crop productivity over a range of conditions (Toivonen et al., 1982).

The observation that various agricultural chemicals reduce or prevent visible ozone injury (see Section 6.3.2.3.2) leads to their use as a means of estimating the impact of ambient ozone on crop production. Field studies with the systemic fungicide, benomyl, showed that it reduced foliar injury 75 to 80 percent in ozone-sensitive bean cultivars but had no effect on the slight injury of the more tolerant cultivar (Manning et al., 1974). Measured for the duration of the study (June through mid-September, about 2540 hr), ozone equaled or exceeded 0.04 ppm for 351 hr (about 14 percent of total hours) during a 40-day period. The concentration equaled or exceeded 0.08 ppm for 27 hr (about 1 percent of total hours). Treatment with benomyl increased the yield of the ozone-sensitive tempo bean by 41 percent; there was no statistical difference in the yield of tenderwhite, an ozone-resistant cultivar, exposed with or without fungicide treatment.

Ethylenediurea (EDU), an experimental chemical not commercially available, was developed specifically as a chemical protectant for ozone (Carnahan et al., 1978). It has been used extensively for reducing visible ozone injury in greenhouse and field studies (see Section 6.3.2.3.2), as well as for estimating ozone-induced yield losses. To estimate ozone-induced yield loss, some plots are treated with EDU and others are not; both types of plots experience the same environmental conditions and ozone exposure. The higher yield in plots treated with EDU is thought to represent the yield that would occur in the absence of ozone, and the yield from the plots not treated with EDU represents the yield in the presence of ozone. Consequently, the impact of ozone on yield is determined by comparing the yield data from plots with and without EDU.

In onions, EDU treatment has been shown to reduce foliar injury and increase plant yield 37.8 percent (Wukasch and Hofstra, 1977a,b). During the study period, July 7 to August 25, the ozone concentration exceeded 0.15 and 0.08 ppm on 5 separate days at each concentration. During a tomato study (June through August), the ozone concentration exceeded 0.08 ppm on 15 days, reaching a maximum of 0.14 ppm (Legassicke and Ormrod, 1981). Treatment with EDU increased the yield of Tiny Tim tomato about 30 percent but had no effect on the New Yorker cultivar.

During 1977 and 1978, EDU was used to estimate the impact of ambient ozone on the yield of three white bean cultivars (Toivonen et al., 1982). Substantial foliar ozone symptoms were observed, and ozone-induced yield losses reached 35 percent in 1977. During 1978, a mid-season drought occurred, resulting in less visible injury, and yield losses reached only 19 percent even though the ozone levels were higher than in 1977. Another study with white bean showed that EDU treatment increased crop yield approximately 24 percent and delayed defoliation (Temple and Bisessar, 1979). The daylight average ozone concentrations (0600 to 2000 hours) were 0.042, 0.042, and 0.028 ppm for June, July, and August, respectively. During these months, the ozone concentration exceeded 0.08 ppm on 11 days for a total of 34 hr.

At a tobacco study plot in southern Ontario during the summer of 1982, the ozone concentrations exceeded 0.08 ppm 14 times, with a maximum of 0.126 ppm (Bisessar and Palmer, 1984). Treatment with EDU reduced foliar injury and increased above-ground plant biomass by about 18 percent.

Greenhouse studies with potato showed that EDU treatment reduced foliar ozone injury and increased the yield of an ozone-sensitive potato cultivar (Foster et al., 1983a). More important, the studies showed that in the absence of ozone EDU had no significant effect on plant growth and yield, indicating that estimates of ozone-induced yield losses are not confounded, at least for potato, by effects of the chemical directly on yield. In southern Ontario, EDU increased the yields of Norchip potato 35.5 percent (Bisessar, 1982). The daylight average ozone concentrations (0600 to 2000 hours) were 0.040, 0.044, and 0.027 ppm for June, July, and August, respectively. During these months, the ozone concentration exceeded 0.08 ppm on 18 days, for a total of 68 hr; and reached a maximum of 0.138 ppm. In New Jersey, EDU studies showed that ambient ozone reduced the yields of Norland potatoes about 25 percent in two separate years (1978 and 1980), and the yield of Norchip potato was significantly reduced (10 percent) in 1980 (Clarke et al., 1983). The yield of the ozone-resistant cultivar was not improved by EDU treatment. During these 2 years (1978 and 1980), the ambient oxidant doses were 65 and 110 ppm-hr, which is equivalent to mean ozone concentrations of approximately 0.030 and 0.051 ppm for the study period. A 3-year field study (in southern Canada) using three potato cultivars found that plants treated with EDU did not yield better than untreated plants (Holley et al., 1985). During the study period (July 1 to August 31) the O_3 concentration exceeded 0.08 ppm for 62 (1980), 18 (1981), and 26 (1982) hours. Although EDU treatment did not increase yield, it did reduce foliar O_3 injury. The authors concluded that the ambient O_3 concentrations were too low and the resultant severity of injury was too small to have a significant effect on yield. A combined treatment with EDU and a fungicide (Du-Ter) significantly increased yield. The fungicide apparently prevented the early blight pathogen, Alternaria solani, from colonizing the O_3-induced foliar lesions. This study demonstrates that O_3 can render the plant more sensitive to biotic stresses which, in this case, subsequently induced the yield loss.

The results of the above studies show that chemical protectants can improve crop yield and can be used to provide estimates of ozone-induced crop loss on several crop species. The data clearly show that the ozone concentrations occurring during these studies were sufficiently high to reduce crop yields 10 to 40 percent, even though there were few times when the ozone concentrations exceeded 0.08 ppm.

6.4.3.2.1.3 Other field studies. Low concentrations of O_3 added to filtered air in field chambers induced yield reductions in a variety of plant species (Table 6-21). Alfalfa exhibited a 49 percent decrease in top dry weight when exposed to 0.05 ppm of O_3 for 68 days (Neely et al., 1977). Extended (several weeks) exposures to 0.10 ppm caused yield reductions in alfalfa (Neely et al., 1977), soybean (Heagle et al., 1974), sweet corn (Heagle et al., 1972), and ponderosa and western white pine seedling (Wilhour and Neely, 1977). Stem specific gravity, an indicator of wood density and quality, of several hybrid poplar clones was consistently less in response to 0.15 ppm of O_3 12 hr/day for 102 days; but effects on height ranged from slight stimulations in four clones to a significant reduction in one clone (Patton, 1981).

6.4.3.2.1.4 Greenhouse and indoor chamber studies. The effects of O_3 on plant yield may be mediated by a myriad of genetic, cultural, and environmental factors (see Section 6.3). The previously discussed studies have attempted to

TABLE 6-21. EFFECTS OF OZONE ADDED TO FILTERED AIR IN FIELD CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control[b]	Monitoring method[c]	Calibration method[d]	Fumigation facility[e]	Reference
Alfalfa	0.05	7 hr/day, 68 days	31, top dry wt, 1st harvest; 49[f] top dry wt, 2nd harvest 17, total protein, top, 1st harvest; 42[f], total protein, top, 2nd harvest 32[f], total nonstructural carbohydrate (TNC), 1st harvest (top) 55[f], total nonstructural carbohydrate (TNC), 2nd harvest (top)	Mast	Known O_3 source 1% NBKI	FC-CT	Neely et al. (1977)
Alfalfa	0.10	7 hr/day, 70 days	51[f], top dry wt, final harvest 53[f], total nonstructural carbohydrate (TNC), final harvest 38[f], total protein, final harvest	Mast	Known O_3 source,	FC-CT 1% NBKI	Neely et al. (1977)
Soybean (Dare)	0.05 0.10	6 hr/day, 133 days	3, seed wt/plant 55[f], seed wt/plant	Mast	2% NBKI	FC-CT	Heagle et al. (1974)
Sweet corn (Golden midget)	0.05 0.10	6 hr/day, 64 days	9, kernel dry wt 45[f], kernel dry wt	Mast	2% NBKI	FC-CT	Heagle et al. (1972)
(White midget)	0.05 0.10	6 hr/day, 71 days	0				
Douglas fir	0.10	6 hr/day, 126 days	6, height; 15, stem dry wt	Mast	Known O_3 source, 1% NBKI	FC-CT	Wilhour and Neely (1977)
Jeffrey pine	0.10		2, height; 2, stem dry wt				
Lodgepole pine	0.10		8, height, 8, stem dry wt				
Monterey pine	0.10		0, height; 0, stem dry wt				

TABLE 6-21 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR IN FIELD CHAMBERS ON THE YIELD OF SELECTED CROPS[a]

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control[b]	Monitoring method[c]	Calibration method[d]	Fumigation facility[e]	Reference
Ponderosa pine	0.10	6 hr/day, 126 days	11, height, 21[f], stem dry wt	Mast	Known O_3 source, % NBKI	FC-CT	Wilhour and Neely (1977)
Shore pine	0.10		2, height; 6, stem dry wt				
Sugar pine	0.10		0, height; 0, stem dry wt				
Western white pine	0.10		0, height, 9[f], stem dry wt				
Sitka spruce	0.10		0, height, 14, stem dry wt				
Hybrid poplar (252)	0.15	12 hr/day, 102 days	+16, height; 12[f], stem specific gravity	UV	Known O_3 source	OT	Patton 1981
(279)	0.15		23, height; 14[f], stem specific gravity				
(346)	0.15		3, height; 6[f], stem specific gravity				
(W5)	0.15		5, height; 12[f], stem specific gravity				
(W87)	0.15		+19, height; 11[f], stem specific gravity				
Hybrid poplar (42)	0.15		25, height; 8, stem specific gravity				
(50)	0.15		58[f], height; 1, stem specific gravity				
(207)	0.15		+8, height; 7[f], stem specific gravity				
(215)	0.15		+17, height; 11, stem specific gravity				

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[a] Where a column entry is blank the information is the same as above.

[b] + = an increase above the control.

[c] Mast = Mast meter (coulometric); UV = ultraviolet spectrometry.

[d] NBKI = neutral buffered potassium iodide.

[e] OT = open-top chamber; FC-CT = closed-top field chamber.

[f] Significant at $p = 0.05$

quantify plant responses to O_3 under ambient or normal environmental and cultural conditions. Several investigations on the yield responses of plants to O_3 have been performed under more controlled (to various degrees) conditions (Tables 6-22, 6-23). These exposures at 0.041 to 0.40 ppm of O_3 will be discussed as they relate to the previous studies.

Ozone caused significant yield reductions in exposures lasting several weeks (Table 6-23). At O_3 concentrations of 0.05 ppm or greater, the response varied among species. Hybrid poplar cuttings exhibited a 13-fold increase in leaf abscission in response to 0.041 ppm for 5 months (Mooi, 1980). There was a significant 14 percent increase in height accompanied by a slight decrease in stem dry weight. American sycamore seedlings exhibited a significant 9 percent height reduction (Kress et al., 1982b), and loblolly pine seedlings showed 18 percent height reduction (Kress and Skelly, 1982) at 0.05 ppm for 4 wk. Yellow poplar and white ash seedlings exhibited significant 60 percent and 22 percent increases in height and total dry weight, respectively, following identical exposures (Kress and Skelly, 1982). In general, slight growth stimulations by O_3 are more common in hardwood tree species than in coniferous tree species (Kress and Skelly, 1982) (Table 6-23).

Significant yield reductions were noted for many species exposed to 0.05 to 0.10 ppm of O_3 for one to several weeks (Tables 6-22, 6-23). Carnations had significantly fewer flowers and flower buds when grown in air containing 0.05 to 0.09 ppm of O_3 for 24 hr/day for 12 to 56 days (Feder and Campbell, 1968). Pasture grasses produced less top growth when exposed to 0.09 ppm of O_3 for 4 hr/day for 5 wk (Horsman et al., 1980). Exposure-response equations were developed for three fescue cultivars under greenhouse conditions (Flagler and Youngner, 1982a). The cultivar Kentucky 31 showed the largest yield decrease with increasing O_3 concentration; based on yield data it was ranked most sensitive and Fawn the least sensitive of the three. Significant yield reductions (10 percent) were predicted for each of the cultivars at the following O_3 concentrations (ppm): 0.119 (Kentucky 31), 0.10 (Alta), and 0.11 (Fawn). The cultivars were exposed for 6 hr/day, 1 day/wk for 7 wk. Significant yield reductions have been noted for alfalfa (Hoffman et al., 1975); clover (Blum et al., 1982), and loblolly pine, pitch pine, sweetgum, American sycamore, and green ash (Kress and Skelly, 1982) when exposed to 0.10 ppm of O_3 for various lengths of time. Numerous studies have reported no significant effects, however, and some have reported yield stimulations. Significant yield stimulations

TABLE 6-22. EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Pinto bean	0.15 0.25 0.35	2 hr/day, 63 days	44[ng], pod fresh wt 100[ng], pod fresh wt 100[ng], pod fresh wt	Mast	Not given	Room	Hoffman et al. (1973)
Sweet corn (Golden jubilee)	0.20 0.35	3 hr/day, 3 days/ wk, 8 wk	13[e], ear fresh wt; 13[e], kernel dry wt; +1300[e], length of ear with shrivelled kernals	Mast	2% NBKI	GH	Oshima (1973)
	0.35	3 hr/day, 3 days/ wk, 8wk	22[e] kernel dry wt				
Wheat (Arthur 71)	0.20	4 hr/day, 7 days	30[e], seed yield; 17[e], kernel wt; 8, % seed set	Mast	Not given	GC	Shannon and Mulchi (1974)
(Blueboy)	0.20	4 hr/day, 7 days	24, seed yield; 2, kernel wt; 22[e], % seed set				
Radish (Cherry belle)	0.20 0.40	3 hr or 6 hr	6[ng], root fresh wt; 6[ng], root dry wt 38[ng], root fresh wt; 40[ng], root dry wt	Chem	Known O_3 source	CH-CSTR	Reinert and Gray (1981)
Radish (Cavalier)	0.25	3 hr	33[e], root dry wt (average of 4 pre- or post-fumigation temperature regimes)	Mast	Not given		Adedipe and Omrod (1974)
(Cherry belle)	0.25	3 hr	37[e], root dry wt (average of 4 pre- or post-fumigation temperature regimes)				
Beet	0.20	0.5 hr/day, 38 days 1 hr/day, 38 days 2 hr/day, 38 days 3 hr/day, 38 days	+9, storage root dry wt +2, storage root dry wt 40[e], storage root dry wt 40[e], storage root dry wt	Mast	Not given	GC	Ogata and Maas (1973)

TABLE 6-22 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Potato (Norland)	0.20	3 hr/day, every 2 wk, 120 days	20[e], tuber no.; 25[e], tuber wt; 13[e], total solids	Not given	Not given	GC	Pell et al. (1980)
(Kennebec)	0.20	3 hr/day, every 2 wk, 140 days	36[e], tuber no.; 42[e], tuber wt; 20[e], total solids				
Pepper (M-75)	0.12 0.20	3 hr/day, 3 day/wk, 11 wk	19[e], dry wt/fruit; 20, no. mature fruit; 50[e], dry wt/fruit; 53[e], no mature fruit	Mast	UV	CH	Bennett et al. (1979)
Tomato (Walter)	0.20	4 hr/day, 2 day/wk, 13 wk	6, fruit fresh wt	Chem	Known O_3 source	GH-CSTR	Shew et al. (1982)
Cotton (Acala SJ-2)	0.25 0.25	6 hr/day, 2 day/wk, 13 wk, 6 hr/day, 2 day/wk, 18 wk	52[e], no. of bolls; 62[e], fiber dry wt; 55[e], no. of bolls; 59[e], fiber dry wt	UV	UV	CH	Oshima et al. (1979)
Carnation (White sim)	0.05-0.09	24 hr/day, 12 days 23 days 44 days 56 days	74[e], no. of flower buds 53[e], no. of flower buds 46[e], no. of flower buds 100[e], no. of normal open flowers	Mast	Not given	GH	Feder and Campbell (1968)
Coleus (Pastel rainbow)	0.10 0.20 0.40	2 hr 2 hr 2 hr	+3, flower no. 4, flower no. 8[e], flower no.	Mast	Not given	CH	Adedipe et al. (1972)
Snapdragons (Rocket mixture)	0.10 0.20 0.40	2 hr 2 hr 2 hr	+1, flower no. 10, flower no. 9, flower no.	Mast	Not given	CH	
(Floral carpet formula mixture)	0.10 0.20 0.40	2 hr 2 hr 2 hr	+3, flower no. 2, flower no. 4, flower no.	Mast	Not given	CH	

TABLE 6-22 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Begonia (Linda)	0.10	2 hr	4, flower no.	Mast	Not given	CH	Adedipe et al. (1972)
	0.20	2 hr	9, flower no.				
	0.40	2 hr	5, flower no.				
(Scarletta)	0.10	2 hr	+5, flower no.	Mast		CH	
	0.20	2 hr	+3, flower no.				
	0.40	2 hr	8[e], flower no.				
(White Tausendschon)	0.10	2 hr	5, flower no.	Mast		CH	
	0.20	2 hr	10, flower no.				
	0.40	2 hr	10, flower no.				
Petunia (Canadian All Double Mixture)	0.10	2 hr	0, flower no.	Mast		CH	
	0.20	2 hr	4, flower no.				
	0.40	2 hr	7, flower no.				
(Capri)	0.10	2 hr	7, flower no.	Mast		CH	
	0.20	2 hr	6, flower no.				
	0.40	2 hr	14[e], flower no.				
(Bonanza)	0.10	2 hr	+3, flower no.	Mast		CH	
	0.20	2 hr	8, flower no.				
	0.40	2 hr	10, flower no.				
Coleus (Scarlet Rainbow)	0.10	2 hr	+3, flower no.	Mast		CH	
	0.20	2 hr	20[e], flower no.				
	0.40	2 hr	28[e], flower no.				
Begonia (Schwabenland red)	0.25	4 hr/day, 4 times once every 6 days	39[e], flower wt; (54% foliar injury)	Chem	Not given	GH-CSTR	Reinert and Nelson (1980)
(Whisper-O-pink)	0.25	4 hr/day, 4 times once every 6 days	22[e], flower wt; (25% foliar injury)	Chem		GH-CSTR	

TABLE 6-22 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control^{a}	Monitoring method^{b}	Calibration method^{c}	Fumigation facility^{d}	Reference
(Fantasy)	0.25	4 hr/day, 4 times once every 6 days	6^{e}, flower wt; (2% foliar injury)	Chem	Not given	GH-CSTR	Reinert and Nelson (1980)
(Renaissance)	0.25		55^{e}, flower wt; (15% foliar injury)	Chem		GH-CSTR	
(Turo)	0.25		+10, flower wt; (8% foliar injury)	Chem		GH-CSTR	
Alfalfa (Moapa)	0.10 0.15 0.20	2 hr/day, 21 days 2 hr/day, 21 days 2 hr/day, 21 days	16^{e}, top dry wt 26^{e}, top dry wt 39^{e}, top dry wt	Mast	Not given	CH	Hoffman et al. (1975)
Alfalfa (Moapa)	0.10 0.10	2 hr/day, 21 days 2 hr/day, 42 days	21^{e}, top dry wt 20^{e}, top dry wt	Mast		CH	
Pasture grass (N.Z. grasslands)	0.09	4 hr/day, 5 days/wk, 5 wk	20^{e}, top dry wt	Chem	Not given	GC	Horsman et al. (1980)
(Victorian)	0.09	4 hr/day, 5 days wk, 5 wk	14^{e}, top dry wt	Chem		GC	
(Australian)	0.09	4 hr/day, 5 days wk, 5 wk	18^{e}, top dry wt	Chem		GC	
Ladino clover (Tillman)	0.10	6 hr/day, 5 days	20^{e}, shoot dry wt; 38^{e}, shoot total nonstructural carbohydrate (TNC)	Chem	2% NBKI	GH-CH	Blum et al. (1982)
Tall fescue (Alta)	0.10 0.20 0.30 0.40	6 hr/day, 1 day/wk, 7 wk 6 hr/day, 1 day/wk, 7 wk	10, dry wt/plant 20, dry wt/plant 30, dry wt/plant; significant linear regression: r=0.98	UV	UV	GH-CSTR	Flagler and Youngner (1982a)

TABLE 6-22 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % reduction from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
(Fawn)	0.10	6 hr/day, 1 day/wk, 7 wk	9, dry wt/ plant	UV	UV	GH-CSTR	Flagler and Youngner (1982a)
	0.20		18, dry wt/plant significant linear				
	0.30	6 hr/day, 1 day/wk, 7 wk	36, dry wt/plant regression, r = 0.99				
	0.40	6 hr/day, 1 day/wk, 7 wk					
(Kentucky-31)	0.10	6 hr/day, 1 day/wk, 12 wk	13, dry wt/plant				
	0.20		27, dry wt/plant significant linear				
	0.30	6 hr/day, 1 day/wk, 12 wk	40, dry wt/plant regression, r = 0.98				
	0.40		54, dry wt/plant				
Tall fescue (Alta)	0.10		+3, top dry wt	UV	UV	CH-CSTR	Flagler and Youngner, (1982b)
	0.20		19, top dry wt				
	0.30		41, top dry wt				

[a] + = an increase above the control; ng = statistical data not given.

[b] Chem. = chemiluminescence; Mast = Mast meter (coulombmetric); UV = ultraviolet spectrometry.

[c] NBKI = neutral buffered potassium iodide.

[d] GH = greenhouse; CSTR = continuous stirred tank reactor; GH=CSTR = CSTR in greenhouse; GC = controlled environment growth chamber; CH = manufactured chamber other than CSTR or GC; GH-CH = CH in greenhouse; Room = plant growth room.

[e] Significant at $p = 0.05$.

TABLE 6-23. EFFECTS OF OZONE ADDED TO FILTERED AIR ON THE YIELD OF SELECTED TREE CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Poplar (Dorskamp)	0.041	12 hr/day, 5 mo	+14[e], stem length; 12 stem dry wt; +1333, no. of dropped leaves; 6, total dry wt	Chem	NBKI	GH-CH	Mooi (1980)
(Zeeland)	0.041	12 hr/day, 5 mo	2, stem length; 4, stem dry wt; +692, no. of dropped leaves; 0, total dry wt	Chem	NBKI	GH-CH	Mooi (1980)
American Sycamore (16-SYC-19)	0.05	6 hr/day, 28 days	9[e], height growth	Chem	1% NBKI	CH	Kress et al. (1982b)
(16-SYC-23)	0.05	6 hr/day, 28 day	2, height growth				
American Sycamore (16-SYC-19)	0.05	6 hr/day, 28 days	11, height growth	Chem	1% NBKI	CSTR	Kress et al. (1982b)
(16-SYC-23)	0.05	6 hr/day, 28 day	9[e], height growth				
Sweetgum	0.05 0.10 0.15	6 hr/day, 28 days	+9, height growth; 10, total dry wt 29[e], height growth; 26, total dry wt 45[e], height growth; 42[e], total dry wt	Chem	Constant source, NBKI, UV	CSTR	Kress and Skelly (1982)
American Sycamore	0.05 0.10 0.15	6 hr/day, 28 days	+4, height growth; 23, total dry wt 27[e], height growth; 61[e], total dry wt 21[e], height growth; 69[e], total dry wt	Chem	Constant source, NBKI, UV	CSTR	
White ash	0.05 0.10 0.15	6 hr/day, 28 days	+12, height growth; +22[e], total dry wt 9, height growth; 9, total dry wt 15, height growth; 17[e], total dry wt	Chem	Constant source, NBKI, UV	CSTR	Kress and Skelly (1982)
Green ash	0.05 0.10 0.15	6 hr/day, 28 days	2, height growth; 14, total dry wt 24[e], height growth, 28, total dry wt 30[e], height growth; 33, total dry wt	Chem	Constant source, NBKI, UV	CSTR	Kress and Skelly (1982)

TABLE 6-23 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON YIELD OF SELECTED TREE CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Willow oak	0.05	6 hr/day, 28 days	1, height growth; 2, total dry wt	Chem	Constant source, NBKI, UV	CSTR	Kress and Skelly (1982)
	0.10		4, height growth; 11, total dry wt				
Sugar maple	0.05	6 hr/day, 28 days	5, height growth; 2, total dry wt	Chem		CSTR	Kress and Skelly (1982)
	0.10		$+8^{e}$, height growth; 7^{e}, total dry wt				
	0.15		12^{e}, height growth; 41^{e}, total dry wt				
Yellow poplar	0.05	6 hr/day, 28 days	$+60^{e}$, height growth; +41, total dry wt	Chem		CSTR	
	0.10		+8, height growth; +5, total dry wt				
	0.15		12, height growth; +18, total dry wt				
Yellow poplar	0.10	12 hr/day, 48 days	19^{ng}, relative growth rate	Chem	Not given	CSTR	Jensen (1981)
Cottonwood	0.10		59^{ng}, relative growth rate				
White ash	0.10		no significant effects				
White ash	0.10	4 hr/day, 1 day/wk, 9 wk	+13, total height; +7, shoot dry wt	Not given	Not given	Not given	McClenahen, (1979)
	0.20		0, total height; +5, shoot dry wt				
	0.30		0, total height; 11, shoot dry wt				
	0.40		0, total height; 14, shoot dry wt				
Black cherry	0.10		+16, total height; +15, shoot dry wt	Not given	Not given	Not given	McClenahen, (1979)
	0.20		+5, total height; 4, shoot dry wt				
	0.30		+3, total height; 4, shoot dry wt				
	0.40		28^{e}, total height; 15, shoot dry wt				
Hybrid poplar (NS 207 + NE 211)	0.15	8 hr/day, 5 days/wk, 6 wk	50^{e}, dry wt new shoots from terminal cuttings 62^{e}, dry wt new shoots from basal cuttings	Not given	Not given	GH-CH	Jensen and Dochinger (1974)

TABLE 6-23 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Hybrid poplar (207)	0.20 0.20	7.5 hr/day, 5 day/wk, 6 wk	5, height 8, height	Not given	Not given	CH	Jensen (1979)
Yellow birch	0.25	8 hr/day, 5 day/wk,	9, height 15 wk	MAST	NBKI	GH-CH	Jensen and Masters (1975)
White birch	0.25		34, height				
Bigtooth aspen	0.25		+7, height				
Eastern cottonwood	0.25						
Red maple (163 ME)	0.25	8 hr/day, 6 wk	18, height	MAST	1% NBKI	CH	Dochinger and Townsend (1979)
(167 NB)			32, height				
(128 OH)			37^e, height				
Loblolly pine (4-5 x 523)	0.05	6 hr/day, 28 days	6, height growth	Chem	1% NBKI	CH	Kress et al. (1982a)
(14-5 x 517)	0.05						
Loblolly pine	0.05 0.10 0.15	6 hr/day, 28 days	18^e, height growth; 14, total dry wt 27^e, height growth; 22^e, total dry wt 41^e, height growth; 28^e, total dry wt	Chem	Constant source, NBKI, UV	CSTR	Kress and Skelly (1982)
Pitch pine	0.05 0.10 0.15	6 hr/day, 28 days	4, height growth; 8, total dry wt 13^e, height growth; 19, total dry wt 26^e, height growth; 24^e, total dry wt				

TABLE 6-23 (cont'd). EFFECTS OF OZONE ADDED TO FILTERED AIR ON YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Yield, % from control[a]	Monitoring method[b]	Calibration method[c]	Fumigation facility[d]	Reference
Virginia pine	0.05	6 hr/day, 28 days	5, height growth; +2, total dry wt	Chem	Constant source, NBKI, UV	CSTR	Kress and Skelly (1982)
	0.10		11, height growth; 3, total dry wt				
	0.15		14, height growth; 13, total dry wt				
White spruce	0.25	8 hr/day, 5 day/wk, 15 wk	5, height	Mast	NBKI	GH-CH	Jensen and Masters (1975)
Japanese larch	0.25		+6, height	Mast	NBKI	GH-CH	

[a] + = an increase above the control; ng = statistical data not given.

[b] Chem. = chemiluminescence; Mast = Mast meter (coulometric); UV = ultraviolet spectrometry.

[c] NBKI = neutral buffered potassium iodide.

[d] GH = greenhouse; CSTR = continuous stirred tank reactor; CH = manufactured chamber other than CSTR or GC; GH-CH = CH in greenhouse.

[e] Significant at $p = 0.05$.

in response to 0.10 ppm of O_3 for 6 hr/day for 4 wk have been noted for sugar maple (Kress and Skelly, 1982).

It is difficult to extrapolate data from studies conducted under more controlled conditions (greenhouse, growth chamber) to field conditions, except when plants are normally grown under these conditions (e.g., flower crops). The more controlled chamber data can serve, however, to strengthen the demonstration of O_3 effects in the field. Concentrations of 0.05 ppm of O_3, in extended or repeated exposures, have been shown to cause yield reductions in some species or cultivars, no effects in others, and increased yield in others. Concentrations of 0.10 ppm and above more consistently cause yield reductions, although exceptions can be found (Tables 6-21, 6-22, 6-23).

6.4.3.2.1.5 Effects of ozone on crop quality. Quality is a broad term that includes many features such as chemical composition, physical appearance, taste, and ability to withstand storage and transport. All these features have economic importance.

Four types of experimental approaches were used to investigate the effects of O_3 or oxidants on crop quality: (1) field experiments in which the impact of ambient oxidants and charcoal-filtered air were contrasted; (2) field experiments in which ambient oxidant injury was prevented by using an antioxidant chemical spray; (3) field experiments in which O_3 was added to ambient or charcoal-filtered air; and (4) laboratory experiments in which potential effects were measured by exposing plants to O_3.

The effects of ambient oxidants were studied at three different locations (Riverside, California; Geneva, New York; and Beltsville, Maryland) to determine their impact on the quality of alfalfa, grape, and soybean, respectively (Thompson et al., 1976b; Musselman et al., 1978; Howell and Rose, 1980). Over a period of 7 harvests, alfalfa plants experienced oxidant concentrations greater than 0.08 ppm between 25 and 60 percent and 0.12 ppm between 5 and 50 percent of daylight hours, respectively (measured with a Mast meter). Plants receiving ambient oxidants exhibited significant ($p = 0.05$ or 0.01) changes in a number of quality variables in some harvests. Ambient oxidants decreased crude fiber, β-carotene, and vitamin C; increased niacin; and had no effect on protein efficiency and nitrogen digestibility ratios (Thompson et al., 1976b). Grape crops exposed to ambient oxidants suffered a 6 percent reduction in soluble solids ($p = 0.05$), which would reduce the value of this fruit for wine (Musselman et al., 1978); however, ozone concentrations were not measured at the Fredonia, NY, site where grape experiments were conducted. Soybean seed quality exhibited small but significant ($p = 0.05$) changes; protein was increased 2 percent and oil was decreased 3.8 percent (Howell and Rose, 1980) when the plants were exposed to ambient oxidants at 0.08 ppm or greater for 3 percent of the season and 0.12 ppm or greater for 0.6 percent of the growing season (the experimental conditions for the seed quality study are reported in Howell et al., 1979).

In addition to measuring yield in terms of biomass, some of the NCLAN studies have examined the quality of the yield. Corsoy soybeans exhibited a significant linear decrease ($R^2 = 0.81$) in the percentage of oil content of seeds as the O_3 concentration increased. Concurrently, there was a significant increase in percentage of protein content with increasing O_3 concentration (Kress and Miller, 1983). Estimated changes resulting from a seasonal 7-hr average concentration of 0.10 ppm of O_3 were a 5 percent decrease in oil content and a 4 percent increase in protein content.

Clarke et al. (1983) grew potatoes in ambient air plots in central New Jersey; half the plants were treated with the antioxidant EDU to suppress the effects of O_3. In 1980, the ambient oxidant dose was 110 ppm-hr. Specific gravity, a quality directly correlated with high quality of processed and tablestock potatoes, was 0.4 percent lower in non-EDU-treated plants ($p = 0.05$). In 1978, the ambient oxidant dose was 65 ppm-hr; changes in specific gravity were not detected.

Alfalfa plants exposed to 0.10 ppm of O_3 (7 hr/day for 70 days) showed an increased protein and amino acid content per unit area, but a decrease in total protein and amino acid because of reduced dry matter production (Neely et al., 1977). Reductions were also noted in the β-carotene and total nonstructural carbohydrate.

Small trees from several clones of hybrid poplar have exhibited decreased stem specific gravity (a measure of wood quality that could result in reduced wood strength or reduced pulpwood value) when exposed to 0.15 ppm O_3 for 12 hr/day for 102 days in open-top chambers (Patton, 1981).

A number of investigators have exposed greenhouse-grown crops to controlled doses of O_3 and subsequently measured the impact on crop quality (chemical composition). These results serve more as indicators of potential impact than predictors that effects would occur in a field environment. Results are summarized below.

Pippen et al. (1975) exposed cabbage, carrot, corn, lettuce, strawberry, and tomato to intermittent acute doses of O_3. Ozone concentrations ranged from 0.20 to 0.35 ppm for 2.5 to 6.5 hr, from 1 to 3 days/wk from emergence to harvest. Plants were exposed to O_3 for 1.62 to 3.59 percent of the life cycle, depending on the species. Some of the species studied exhibited significant ($p = 0.05$) changes in quality in response to one or more of the O_3 regimes employed. Corn exhibited a decrease (at 0.20 ppm O_3) in solids, β-carotene, and carbohydrates, but total nitrogen and vitamin C levels increased. The niacin concentration increased in carrots and strawberries. Solids, fiber content, and vitamin C were all reduced in tomato (at 0.35 ppm O_3). Cabbage exhibited significant increases in total solids and vitamin C.

When greenhouse-grown potato plants were exposed to O_3 at a concentration of 0.20 ppm for 3 hr once every 2 wk throughout the growth period, tubers exhibited a decrease in percentage dry matter that is associated with a decrease in fluffiness of tablestock potatoes (Pell et al., 1980). Reducing sugars, associated with undesirable darkening of potato chips, increased in tubers harvested from plants exposed to O_3. Glycoalkaloids, compounds that can cause a bitter taste in potato tubers, either decreased or were unaffected by the O_3 treatment (Speroni et al., 1981).

The potential of O_3 to induce a series of estrogenic isoflavonoids was investigated in five different alfalfa cultivars (Hurwitz et al., 1979; Skärby and Pell, 1979; Jones and Pell, 1981). These biochemicals have been directly correlated with breeding disturbances in both domesticated and wild animal species. Coumestrol, daidzein, genistein, and formononetin, all with potentially adverse affects on crop quality, were not detected in greenhouse-grown alfalfa plants that received O_3 concentrations of 0.20 to 0.40 ppm for 3 hr. Ladino clover, another forage crop, exhibited reduced total nonstructural carbohydrate and generally increased mineral content (except for sodium) when exposed to 0.10 ppm of O_3 (6 hr/day for 5 days) (Blum et al., 1982).

The impact of O_3 and ambient oxidants on crop quality has important implications from both health and economic perspectives. A reduction in nutritional value of food or forage, such as reduced vitamin content or precursors to proteins, will be detrimental to the consumer. An adverse effect on a crop destined for processing, such as grapes for wine or potatoes for chips, will reduce the economic value of the crop. It is difficult at present, however, to correlate completely these effects with the more conventional measures of O_3 effects on foliage and yield.

6.4.3.2.1.6 Effects of ozone on plant reproduction. Ozone has been shown to affect the reproductive capacities of plants. The flowering and seed production of soybean plants was reduced by O_3 at 0.10 ppm (6 hr/day, 133 days) (Heagle et al., 1974). In sweet corn plants, seed production as estimated by percentage of ear filled was reduced when the plants were grown in an environment of 0.10 ppm of O_3 (6 hr/day, 64 days) (Heagle et al., 1972). Wheat plants exposed to 0.20 ppm of O_3 (4 hr/day, 7 days) at anthesis exhibited reduced seed set (Shannon and Mulchi, 1974). Reduced seed production of cotton plants exposed to 0.25 ppm O_3 (6 hr/day, 2 day/wk, 13 wk) was reported (Oshima et al., 1979).

The number of tillers in three tall fescue cultivars increased slightly as O_3 was increased from 0.10 to 0.40 ppm (6 hr/day, 1 day/wk, 7 wk) (Flagler and Youngner, 1982a). These data indicate that O_3 may decrease the reproductive capacity of plants. The reductions in seed production suggest an O_3 impact on fertilization processes. The observation that O_3 (0.05 ppm for 5.5 hr) reduced pollen germination and pollen tube elongation (40 to 50 percent) in tobacco and petunia (Feder, 1968) supports this conclusion. Ozone also reduced the germination of corn pollen 60 (0.06 ppm) and 70 percent (0.12 ppm), respectively (Mumford et al., 1972). Plants were exposed to O_3 (0.06 or 0.12 ppm for 5.5 hr/day for 60 days) and the pollen was harvested daily as soon as it was mature and the percentage germination could be determined. Because the pollen was harvested as soon as it reached maturity, it is probable that the pollen was exposed to O_3 for only a short time period, with the data thus indicating that pollen is quite sensitive to O_3.

6.4.3.2.1.7 Relationship between foliar injury and yield loss. Because plant growth depends on the presence of functional leaves to conduct the photosynthesis required for plant growth, various studies have been conducted to determine the association between foliar injury and yield for species in which the foliage is not part of the yield. Some investigations discussed in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) demonstrated yield loss with little or no foliar injury (Tingey and Reinert, 1975; Tingey et al., 1971a); others demonstrated significant foliar injury not accompanied by yield loss (Heagle et al., 1974; Oshima et al., 1975). Many other studies can be cited to illustrate the inconsistency of the relationship between foliar injury and yield loss when the foliage is not the yield component. Significant yield reductions with no foliar injury have been noted for American sycamore (Kress et al., 1982b), loblolly and pitch pine (Kress and Skelly, 1982), carnations (Feder and Campbell, 1968), and petunia and coleus (Adedipe et al., 1972). With red maple seedlings, foliar injury was directly correlated with subsequent height reductions (Dochinger and Townsend, 1979). The relative sensitivities of two potato cultivars were reversed when judged on yield reductions rather than foliar injury (Pell et al., 1980). In a study comparing the effects of long- and short-term exposures, a long-term exposure (0.15 ppm for 8 hr day, 5 days/wk for 6 wk) resulted in 75 percent foliar injury and 50 percent growth reduction; whereas the short-term exposure (1.0 ppm for 2.4 or 8 hr) resulted in 70 percent foliar injury and no growth reduction (Jensen and Dochinger, 1974).

All of the studies in Table 6-20 reported foliar injury as well as yield responses. For field corn, foliar injury response was at lower concentrations than the yield effects, but with increased O_3 concentration the percentage yield reductions became greater than the percentage foliar injury (Heagle et al., 1979a). For wheat, the increases in foliar injury were generally accompanied by decreases in yield, but foliar injury was not a good predictor of yield reduction. For example, at 0.06 ppm O_3, the wheat cultivar Coker 47-27 had 5 percent foliar injury (compared to the control) and 11 percent yield reduction; but the cultivar Holly had 6 percent foliar injury and 1 percent yield reduction (Heagle et al., 1979c). There were no obvious relationships between foliar injury and shoot fresh or dry weight of spinach (Heagle et al., 1979b). In the soybean study also, relative cultivar foliar injury did not predict relative yield response (Heagle and Letchworth, 1982). The cultivars Bragg and Ransom had equal amounts of foliar injury (35 percent) when exposed to 0.10 ppm of O_3, but Bragg yield increased 4 percent and Ransom yield decreased 20 percent.

The lack of correlation between foliar injury and yield reduction for many crops should not be surprising. Plants have evolved with a reserve capacity to cope with some level of stress. For example, a plant species may develop more leaf area than that needed for maintaining yield. Therefore, O_3 would not be expected to reduce plant yield unless its effects were sufficiently great to make some process limiting for plant yield. Yield would also be reduced if O_3 directly impacted the process limiting growth. Unless either of these two conditions is achieved, the plant might display a biological (phytotoxic) response to O_3 but the yield would not be impaired. For plants in which the foliage, however, is the marketable portion, either for food or ornamental use, a phytotoxic impact on the foliage may reduce the yield without altering the plant weight. These concepts imply that not all impacts of O_3 on plants are reflected in growth or yield reductions. Also, O_3 would not impact plant growth or yield unless it made some process more limiting for growth or yield than the environmental factors that currently were controlling growth. These conditions suggest that there are combinations of O_3 concentration and exposure duration that the plant can experience that will not result in visible injury or reduced plant growth and yield. Numerous studies of many plant responses have demonstrated combinations of concentration and time that did not cause a significant effect.

6.4.3.2.2 Biomass and yield responses from ambient exposures. Determination of the effects of ambient air pollutants directly shows the impact of existing air quality on plant yield in the environment. Two basic types of studies are used to describe the effects of ambient exposures on plants. In one type, field observations are used to develop an association between O_3 exposure and plant response (growth or yield reductions or mortality). In the other type, the difference between plant yield in charcoal-filtered air and in ambient air (which may contain a single major pollutant or several) is used to indicate the impact of the pollutant; and some type of exposure chamber is required for these studies. In either case, plants are exposed to pollutant concentrations at the frequency of occurrence found in the ambient air. When only a single pollutant is present or the study is conducted at a single location, or both, the interpretation of the results is simplified. When the studies are conducted at different locations, however, differences in climatic and edaphic conditions, in addition to the pollutant time series that may influence the results and complicate the interpretation, can occur.

The previous criteria document (U.S. Environmental Protection Agency, 1978) reviewed the effects of O_3 in ambient air (Table 6-24). These studies utilized charcoal filtration in greenhouses or open-top chambers or simply correlated effects with the ambient O_3 concentrations. Leaf injury (sweet corn, tobacco, potato), yield reductions (citrus, grape, tobacco, cotton, potato), and quality changes (grape) were documented. It was concluded that ambient oxidants were causing decreased plant growth and yield.

More recently, studies have also been conducted to evaluate the yield of plants grown in the presence of photochemical oxidants (ambient air) versus charcoal-filtered air (Table 6-25).

TABLE 6-24. EFFECTS OF OXIDANTS (OZONE) IN AMBIENT AIR ON GROWTH, YIELD, AND FOLIAR INJURY IN SELECTED PLANTS

Plant species	Oxidant conc., ppm	Duration of exposure	Plant response, % reduction from control	Location of study
Lemon	>0.10	Over growing season	32, yield 52, yield; leaf drop and other effects	California
Orange	>0.10	148 hr/mo average from March-October, 254 hr/mo average from July-September	54, yield; other reductions found	California
Grape, Zinfandel	$\geq$0.25	Often over May-September growing season	12, yield (first year) 61, yield (second year); increased sugar content 47, yield (third year)	California
Corn, sweet	0.20-0.35	Hourly maximum for 3 to 4 days before injury	67, injury (10 cultivars, 5 unmarketable) 18, injury (13 cultivars) 1, injury (11 cultivars)	California
Bean, white	>0.08	9 hr	Bronze color, necrotic stipple, premature abscission	Ontario, Canada
Tobacco, cultivar Bel W_3	0.02-0.03	6 to 8 hr	Minimal injury	Ohio
Tobacco, cultivar Bel W_3	>0.05	Often over growing season	22, fresh wt, top 27, fresh wt, root	North Carolina
Cotton, cultivar Acula	Ambient	Over growing season	7-20, lint + seed (3 locations, 1972) 5-29, lint + seed (3 locations, 1973)	California
Potato, 4 cultivars[a]	$\geq$0.05	326 to 533 hr (2 yr)	34-50, yield (2 years for 2 cultivars) 20-26, yield (1 year for 2 cultivars)	Maryland
Potato, cultivar Haig	0.15	3 consecutive days	95, injury; leaf area covered	Delaware

[a] Greenhouse studies.

Source: National Research Council (1977).

TABLE 6-25. EFFECTS OF AMBIENT AIR IN OPEN-TOP CHAMBERS, OUTDOOR CSTR CHAMBERS, OR GREENHOUSES ON GROWTH AND YIELD OF SELECTED CROPS

Plant species*	O_3 concn., ppm	Exposure duration	Percent reduction from control	Location of study	Monitoring method[a]	Calibration method[b]	Fumigation facility[c]	Reference
Tomato (Fireball 861 VR)	0.035 (0.017-0.072)	99 day average (0600-2100)	33[d], fruit fresh wt	New York	Mast	NBKI	OT	MacLean and Schneider (1976)
Bean (Tendergreen)	0.041 (0.017-0.090)	43 day average (0600-2100)	26[d], pod fresh wt; 24[d], number of pods		Mast	NBKI	OT	
Snap bean (3 cultivars: Astro, BBL 274, BBL 290)	0.042	3 mo average (0900-2000)	1, pod wt	Maryland	Not given	Not given	OT	Heggestad and Bennett (1981)
Soybean (4 cultivars: Cutler, York, Clark, Dare)	>0.05	31% of hr (8:00 a.m. to 10:00 p.m.) from late June to mid-September over three summers; 5% of the time the concentration was above 0.08 ppm	20[d], seed wt; 10[d], wt/100 +2, % protein content, 4% oil content	Maryland	Mast	NBKI, known O_3 source	OT	Howell et al. (1979) Howell and Rose (1980)
Forbs, grasses, sedge §	0.052	1979, 8 hr/day average 1000-1800), April-September	32, total above ground biomass	Virginia	Chem	Known O_3 source, UV	OT	Duchelle et al. (1983)
	0.051	1980, 8 hr/day average (1000-1800), April-September	20, total above ground biomass	Virginia	Chem			
	0.035	1981, 8 hr/day average (1000-1800), April-Sepbember	21, total above ground biomass					
Snap bean (Gallatin 50)	>0.05	Average 170 hr over 60 days exposure (1972-1974) (6 crops)	+5, pod fresh wt	Maryland	Mast	1% NBKI, Chem	OT.	Heggestad et al. (1980)
(BBL 290)	>0.05	Average 170 hr over 60 days exposure (1972-1974) (6 crops)	14[d], pod fresh wt	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al. (1980)
(Astro)	>0.05	Average 170 hr over 60 days exposure (1972-1974) (6 crops)	3, pod fresh wt	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al. (1980)

TABLE 6-25 (cont'd). EFFECTS OF AMBIENT AIR IN OPEN-TOP CHAMBERS, OUTDOOR CSTR CHAMBERS, OR GREENHOUSES ON GROWTH AND YIELD OF SELECTED CROPS

Plant species	O_3 concn., ppm	Exposure duration	Percent reduction from control	Location of study	Monitoring method[a]	Calibration method[b]	Fumigation facility[c]	Reference
(Astro)	>0.05	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	6, pod dry wt	Maryland	Mast	1% NBKI, Chem	OT	Heggestad et al. (1980)
Snap bean (Gallatin 50)	>0.05	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	+1, pod dry wt	Maryland	Mast	1% NBKI Chem	OT	Heggestad et al. (1980)
(BBL 290)	>0.05	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	10, pod dry wt	Maryland	Mast	1% NBKI Chem	OT	Heggestad et al. (1980)
(BBL 274)	>0.05	Average 160 hr over 60 days exposure (1975-1976) (2 crops)	22^{d}, pod dry wt	Maryland	Mast	1% NBKI Chem	OT	Heggestad et al. (1980)
Sweet corn (Bonanza)	>0.08	58% of hr (0600-2100) between 1 July and 6 September	9^{d}, ear fresh wt; 10^{d}, no. seeds/ear	California	Mast	UV	OT	Thompson et al., 1976a
(Monarch Advance)	0.08		28^{d}, ear fresh wt; 42^{d}%, no. seeds/ear					

[a] Chem = chemiluminescence; Mast = Mast oxidant meter (coulombmetric); UV = ultraviolet spectrometry.

[b] NBKI = neutral buffered potassium iodide; UV = ultraviolet spectrometry.

[c] OT = open-top chamber; CSTR = continuous stirred tank reactor.

[d] Significant at $p = 0.05$.

[e] Total above ground biomass, 3 yr average; NF and open plot versus CF α significant at $p = 0.05$

Ambient ozone (mean concentration of 0.035 ppm daily average, 6:00 a.m. to 9:00 p.m.) induced a significant yield reduction (33 percent) in tomato (MacLean and Schneider, 1976). During the 99-day experimental period, the 1-hr average ozone concentration exceeded 0.08 ppm for 11 percent and 0.10 ppm for 6 percent of the daylight hours. Also, the yield of green beans was reduced (26 percent) by ambient ozone (mean concentration of 0.041 ppm daily average, 6:00 a.m. to 9:00 p.m.) (MacLean and Schneider, 1976). The average yield of four soybean cultivars exposed to ambient ozone in Maryland was reduced an average of 20 percent over the 3-yr period (Howell et al., 1979). Over the study period, the ambient ozone concentration exceeded 0.08 ppm and 0.10 ppm 1.8 and 0.9 percent, respectively, of the daylight hours (8:00 a.m. to 8:00 p.m.). In Riverside, CA, the ambient ozone reduced the yield of two sweet corn cultivars 9 and 28 percent, respectively (Thompson et al., 1976a). The ozone concentration during the daylight hours (6:00 a.m. to 9:00 p.m.) exceeded 0.08 ppm and 0.12 ppm for 58 and 39 percent of the time, respectively. The growth of a mixture of forbs, grasses, and sedges at Big Meadows, Shenandoah National Park, VA, was reduced 32, 20, and 21 percent for the years 1979, 1980, and 1981, respectively (Duchelle et al., 1983). At the study site, the mean ozone concentration (11:00 a.m. to 6:00 p.m.) for the period April through September averaged 0.052, 0.051, and 0.035 ppm over the 3-yr period, respectively. For the same time periods, the total ozone dose was 73.4, 74.2, and 50.5 ppm-hr with 1218, 790, and 390 hr, respectively, when the ozone concentration exceeded 0.06 ppm (11:00 a.m. to 6:00 p.m.). The impact of ambient ozone on the yield of several bean cultivars was studied for several years in Maryland (Heggestad et al., 1980). There were seasonal and yearly variations in the impact of ambient ozone on bean yield, which ranged from a 5 percent increase above the control to a 22 percent yield decrease. In each study, there were extended periods when the ozone concentration exceeded 0.05 ppm.

Early ambient air studies in California, in 1976 and 1977, incorporated multiple locations situated along an ambient O_3 gradient in a portion of the South Coast Air Basin, where phytotoxic pollutants other than O_3 occur only at extremely low concentrations (Oshima et al., 1976; Oshima et al., 1977a). These studies used a modified cumulative O_3 dose (sum of hourly averages above 0.10 ppm for the exposure period, ppm-hr) as a summary exposure statistic (Table 6-26). The dose calculation was further modified in the 1977 study by including only those pollutant concentrations present during daylight hours.

TABLE 6-26. EXPOSURE-RESPONSE FUNCTIONS RELATING OZONE DOSE TO PLANT YIELD[a]

Plant species	Yield equation	Dose, ppm-hr, for predicted 10% yield reduction[b]	Reference
Alfalfa[c] (Moapa 69)	$y = 162.4 - 1.5 \times \text{Dose}$	10.8	Oshima et al. (1976)
Tomato[c] (6718VF)	$y = 9.742 - 0.23 \times \text{Dose}$	4.2	Oshima et al. (1977a)
Potato (Centennial Russet)	$y = 1530 - 15.8 \times \text{Dose}$	9.7	Foster et al. (1983b)
Bean[c] (Red Kidney)	$y = 306.7 - 33.33 \times \log \times \text{Dose}$	>51.6	Oshima (1978)

[a] The studies were conducted in California and plants were exposed to ambient O_3.

[b] For alfalfa and tomato, the hourly averages above 0.10 ppm were summed to complete the seasonal dose. For potato and bean, hourly average O_3 concentrations for the duration of the study were summed to complete the seasonal dose.

[c] The original equation was based on pphm-hr, but for this table the regression coefficient was converted to ppm-hr for consistency with data in the rest of the chapter.

In the 1976 study, the lowest dose was 2.64 ppm-hr, the equivalent of 0.11 ppm for 264 hr (1.26 hr/day) of the 5040-hr season. The highest dose was 55.52 ppm-hr, the equivalent of 0.111 ppm for each hour of the 5040-hr season. Alfalfa yield was reduced (10 percent) at a seasonal dose of 10.8 ppm-hr. Tomatoes were substantially more sensitive than alfalfa. The tomato yield was reduced at a seasonal dose of 4.2 ppm-hr.

Oshima (1978) designed and constructed an exposure facility (modified CSTR) by using chambers enclosed by a Teflon® film to minimize environmental alterations. The exposure system used proportional charcoal filtration of ambient air, thus retaining the ambient exposure properties at several pollutant concentrations. Ozone concentrations were expressed as cumulative dose (sum of hourly averages for the exposure period, ppm-hr) (see Sections 6.2.2.1 and 6.4.3.3). Both Oshima (1978) and Foster et al. (1983b) (Table 6-26) were able to demonstrate yield losses in pot-grown red kidney bean and Centennial Russet potato, respectively, at low concentrations of ambient O_3. Potato yield was reduced (10 percent) at a seasonal dose of approximately 9.7 ppm-hr, but a substantially higher dose (>51.6 ppm-hr) was required to impact the yield of red kidney beans. Many of the ambient concentrations used in both studies were equivalent to ambient concentrations in cleaner regions of California and in the eastern United States.

Several studies have measured various plant effects and attempted to describe associations between ambient O_3 and O_3-injury symptoms or yield responses. Oxidant-induced changes in forest ecosystems of California, Virginia, and Utah are discussed in Chapter 7. Some specific references to these and other areas follow. Increasing O_3 sensitivity of ponderosa pine has been correlated with insect-induced mortality (Cobb and Stark, 1970). Over a 3-yr period, 24 percent of 150 study trees died, 92 percent of which exhibited severe foliar O_3 symptoms. No trees classed as healthy or slightly symptomatic died. In a mixed-conifer stand in the San Bernardino Mountains, radial growth for the 30-yr period 1945 to 1975 decreased an average of 34, 1, and 4 percent in areas with severe, moderate, and no injury, respectively (Kickert et al., 1977). Concentrations of O_3 that "commonly exceeded 0.10 ppm" were associated with foliar injury and defoliation.

Reduced growth of O_3-sensitive eastern white pine appears to be attributable to reduced foliar biomass, which results from shortened needles and premature needle loss (Mann et al., 1980). Ozone reduced annual radial growth of the trees studied by 50 percent. The reduced foliar biomass and foliar symptoms were associated with several episodes of O_3 above 0.08 ppm. White pines exhibiting relatively severe symptoms (chlorosis, tipburn, short needles, premature defoliation) experienced a steady decline in average ring width (71 percent over 15 years) and a loss in capacity for recovery (McLaughlin et al., 1982). The annual radial growth of eastern white pine trees exhibiting symptoms of O_3 stress was 28 percent less than that of trees exhibiting few or no symptoms (Benoit et al., 1982). The data of McLaughlin et al. (1982) and Benoit et al. (1982) should be used with caution, however, since the studies used small sample sizes and the radial increment data were not standardized for tree age. Field studies in the San Bernardino National Forest in California showed that during the last 30 years ambient O_3 may have reduced the height growth of ponderosa pine by 25 percent, annual radial growth by 37 percent, and the total volume of wood produced by 84 percent (Miller et al., 1982) (see Chapter 7).

The research presented in this section demonstrates that ambient O_3 in many areas of this country can reduce plant yield. Although the most severe effects appear to occur in the South Coast Air Basin and the San Bernardino Mountains of California, areas with high ambient O_3 concentrations, other agricultural areas in the nation are impacted as well. Data presented in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) suggested that ambient O_3 reduced yields for orange (54 percent), grape (47 to 61 percent), and cotton (5 to 29 percent). Also, the yield of potatoes growing in the eastern United States was reduced 20 to 50 percent by ambient O_3. More recent research has indicated that similar yield reductions are still occurring throughout the country as the result of ambient O_3 exposures. Recent open-top chamber studies have demonstrated losses in tomato (33 percent), bean (26 percent), soybean (20 percent), snapbean (0 to 22 percent), sweet corn (9 percent), several tree species (12 to 67 percent), and forbs, grasses, and sedges (9 to 33 percent). Still other chamber studies have shown yield reductions in potato (42 percent) exposed to ambient photochemical oxidants. The use of chemical protectants such as EDU has demonstrated yield losses in potatoes ranging from 2 to 31 percent. Correlations of plant yield with ambient O_3 concentrations based on either an O_3 gradient or differential cultivar or species sensitivity have been used to predict ambient yield losses in alfalfa (53 percent), tomato (22 percent), and ponderosa and white pines.

6.4.3.3 Exposure-Response Relationships (Empirical Models)--Empirical exposure response models are mathematical functions that describe a relationship between pollutant exposure and a biological response. These models are very useful because the entire relationship defined between the range of exposures is quantitatively described. This desirable property differentiates the models from the results of descriptive designs described in Section 6.4.3.2. In addition, empirical models are useful as research tools because they succinctly summarize relationships in the form of an equation.

Empirical response models describing plant yield losses from O_3 have two major uses that are distinctly different in theory and requirements.

1. Models are used for crop production forecasting. The unit used in the forecasts is yield per unit land area. Because this is essentially a biological forecast, errors introduced from aggregative methods and the exclusion of environmental, cultural, and edaphic variables must be dealt with if model estimates are to be reliable.

2. Models are used to interface biological systems with economic models. The units used as a measure of effect in an economic model are monetary (profit and loss). These models are driven by economic variables such as input and output substitutions; supply, demand, and associated price fluctuations; and regional linkages. Problems of aggregation methods and impacts of economically important variables are considered in terms of the economic units. Errors introduced by aggregation and exclusion of environmental variables also affect the results obtained by economic models.

The development of empirical models is the first and the least complex step in their use. It is the application of these models that is most apt to be misunderstood.

The available empirical models were developed by using various exposure techniques ranging from ambient gradients to highly controlled laboratory exposures; therefore they have different constraints on their application. Additionally, until the emergence of NCLAN (National Crop Loss Assessment Network) as a multisite effort to develop credible crop-loss assessments, no organized effort to standardize developmental methodology had occurred. The NCLAN program represents the first organized effort to establish defensible crop-loss estimates on a national scale.

Only one empirical model was discussed in the dose-response section of the 1978 criteria document (U.S. Environmental Protection Agency, 1978). The

Heck and Tingey (1971) injury model was used to derive tabular and graphic data predicting O_3 concentrations for specific amounts of foliar injury for a number of species. Most other discussion revolved around the limiting-value concept used to relate O_3 concentrations from the existing data base. Many empirical models have been developed since the 1978 air quality document was published, and such models have expanded to the point that they are commonly used as tools in most areas of air pollution research.

There are different categories of empirical exposure-response models. Physiological models generally are used as research tools to summarize relationships and to provide a quantitative means of comparing responses. Injury models predict leaf response at various levels of exposure, and growth models define biomass accumulation, canopy development, and growth of reproductive organs. Yield response models focus on the economically or biologically essential portion of plant growth.

6.4.3.3.1 Physiological models. This section is included to provide an example of the uses of physiological models in basic research, which is the primary area of their application. Physiological response models are used as effective research tools for summarizing relationships or allowing comparisons among species (Tingey et al., 1976b; Coyne and Bingham, 1981). The slope of linear models offers a convenient means for comparison of plant species or populations within a species. Physiological processes are particularly amenable to quantification with functions. Use of these response models fulfills objectives quite different from those fulfilled by the predictive models required for yield-loss estimates.

6.4.3.3.2 Injury models. Injury models estimate the magnitude of foliar injury incurred from pollutant exposures or, in one case, the concentration of pollutant from the degree of injury (Table 6-27). These models have been used to compare air quality in different geographical areas (Goren and Donagi, 1980; Naveh et al., 1978). Heck and Tingey (1971) developed a model that would estimate the O_3 concentration required to cause specific amounts of foliar injury (Table 6-27). This model was the source of tabular and graphic data presented in the dose-response section of the previous ozone criteria document (U.S. Environmental Protection Agency, 1978).

A major contribution to the evolution of injury models was the model developed by Larsen and Heck (1976). They presented a mathematical model based on the assumption that percentage leaf injury was distributed lognormally as a function of pollutant concentration for a specific exposure duration.

TABLE 6-27. SUMMARY OF MODELS DESCRIBING THE RELATIONSHIP BETWEEN FOLIAR INJURY AND OZONE EXPOSURE

Model	Plant species	Reference
1. $y = a + bx$ y = injured leaves, area (%) x = ozone index (ppb x hr) a = -3.5 (winter), -0.38 (summer), -1.85 (fall)[a] b = 0.0037 (winter), 0.0016 (summer), 0.0015 (fall)[a]	Tobacco Bel-W3 Winter $R^2 = 0.94$ Summer R^2 0.98	Goren and Donagi (1980)
2. $P = P_k(1-e^{-kt})$ P = % injured leaves at time t P_k = equilibrium % of injured leaves k = constant determined by least squares	Tobacco Bel-W3 No correlation coefficient available	Naveh et al. (1978)
3. $C = A_0 + A_1I + A_2/t$ C = ozone concentration A_0, A_1, A_2 = regression coefficients I = percent foliar injury t = time of exposure	Selected species Range of R^2 = 0.85 to 0.35	Heck and Tingey (1971)
4. $Z = [-\ln(Mghr) - p(\ln(t)) + (n(C)]/\ln(Sg)$ Z = no. of standard deviations that the percentage of injury is from the median C = ozone concentration t = exposure duration Mghr = geometric mean concentration Sg = standard geometric deviation p = slope of the line on a logarithmic scale.	Selected species Range of R^2 = 0.96 to 0.58	Larsen and Heck (1976)
5. Model 5 Probit $(y) = 1.3 \ln(c) + 0.49 \ln(d) + 0.77$ where c = concentration in µl/l d = duration in hr y = % leaf surface injured	Soybean cv. Hodgson $R^2 = 0.84$	Pratt and Krupa (1981)

TABLE 6-27 (cont'd). SUMMARY OF MODELS DESCRIBING THE RELATIONSHIP BETWEEN FOLIAR INJURY AND OZONE EXPOSURE

Model	Plant species	Reference
6. Model 5 $PIF = 0.2174 + 2.2457 \ln(c) + 2.1378 \ln(t)$ where c = concentration in μl/l t = duration in hr PIF = Probit mean proportion of injured foliage/plant	Black cherry $R^2 = 0.77$	Davis et al. (1981)
7. Short-term controlled fumigations $S = n (\ln(D)) + K$ where $D = (C^{m/n} \times t)$ and S is in the range 0 to 1 S = plant injury degree[b] C = concentration in ppm t = exposure duration in hr m = constant n = constant K = constant $S = 0.278 \ln(D) + 0.999$	Morning glory $R^2 = 0.97$	Nouchi and Aoki (1979)
8. Ambient conditions $S = n \ln(D) + A \ln(D')) + K'$ where $D = \Sigma_i C_i^{m/n}$ S = plant injury degree[b] C_i = hourly average concentration at the ith hour in ppm $A (\ln(D'))$ = contribution to the injury on the current day due to the effects of oxidant dosage up to the previous day A = constant K' = constant	Morning glory $R^2 = 0.70$	Nouchi and Aoki (1979)
$S = 0.278 \ln(D_j) + 0.041 [\ln(D_{j-1}) + \ln(D_{j-2}) + \ln(D_{j-3})] + 1.872$		

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[a] Half the accumulating sum of average hourly O_3 concentration between the first value $\geq$ 40 ppb and the last value $\leq$ 40 ppb.

[b] Plant injury degree = (Σ% damaged leaf per leaf)/Σ area of the leaves that can be damaged to the maximum degree.

This model also has been used for black cherry (Davis et al., 1981) and Hodgson soybean (Pratt and Krupa, 1981). Both groups of investigators modified the Larsen and Heck model slightly by using a probit transformation of the dependent variable.

Nouchi and Aoki (1979) developed injury models for both short-term controlled exposures and long-term ambient exposures with morning glory (Table 6-27). They recognized that foliar injury did not have a linear relationship with the conventional dose statistic (concentration x time) and developed a powered dose (dose raised to some power) for the acute exposure model. Further, Nouchi and Aoki included a factor in the ambient model that incorporated the time-dependent contribution of previous O_3 exposures and modified the dose expression to account for the long-term variable exposures that characterize ambient O_3 episodes. These investigators were the only group that attempted to account for the effects of previous O_3 exposures on foliar injury in their model.

6.4.3.3.3 Growth models. Only a few empirical growth models quantify O_3-induced alterations in biomass accumulation and assimilate partitioning. Oshima et al. (1978; 1979) developed growth models for parsley and cotton and later refined the cotton model (Oshima and Gallavan, 1980). Growth models are used primarily for research purposes and are included in this report only as an example to indicate progress in quantifying O_3 growth responses.

6.4.3.3.4 Yield and loss models. Yield models are the most sought after and most difficult models to develop. These models are necessary for estimates of production and economic loss because they relate yield directly to pollutant exposure. The number and quality of yield models is increasing rapidly because of increased interest and because of the NCLAN program. Existing models are summarized in Table 6-28. Additional discussion of actual yield responses that were derived from many of these studies is presented in tabular and graphic form in Section 6.4.3.2.

Oshima and his coworkers developed predictive models for estimating yield losses from O_3 in California. Using data from plots along an ambient O_3 gradient in southern California, Oshima et al. (1976) developed both yield and yield-loss models for a clone of Moapa 69 alfalfa (Table 6-28). Multiple-regression techniques were used to test the relative contributions of O_3 dose and meteorological variables to changes in alfalfa yield. Ozone was determined to be the greatest contributor to yield variation when compared to the contributions of the other tested variables. The O_3-yield function was then transformed

TABLE 6-28. SUMMARY OF MODELS OF OZONE YIELD AND LOSS

Model		Crop	Reference
1. (a) Total fresh wt function $y = a + bx$ $y = 162.4 - 0.015x$	y = fresh wt (g/plant) a = intercept x = ozone dose (pphm-hr > 10 pphm)	Alfalfa cv Moapa 69 $R^2 = 0.68$	Oshima et al. (1976)
(b) Loss function Transformed from 1(a) by % loss = $(a - wt)/a \times 100$ % Loss = $-1.068 \cdot 10^{-4} + 9.258 \cdot 10^{-3}x$	x = ozone dose (pphm-hr > 10 pphm)		
2. (a) Marketable fruit $y = [\sin(-0.0076x + 84.2816)]^2$	y = % fruit marketable USDA minimum size x = ozone dose (pphm-hr > 10 pphm)	Tomato VF 6718 $R^2 = 0.85$	Oshima et al. (1977a)
(b) Yield function $y = 9.742 - 0.0023x$	y = container yield based on USDA fruit size and packing configuration x = ozone dose (pphm-hr > 10 pphm)	$R^2 = 0.62$	
(c) Loss function Transformed from 2(b) by % loss = $(a - \text{container yield})/a \times 100$ % Loss = $0 + 0.0232x$	x = ozone dose (pphm-hr > 10 pphm)		
3. (a) $y = a + bx$	y = yield (varies with crop) x = ozone exposure in seasonal 7 hr/day mean ozone concentration (ppm) a = intercept b = slope	Selected crops R^2 statistics are not available	Heagle and Heck (1980)
(b) $y = a + b_0x + b_1x^2$	y = yield (varies with crop) x = ozone exposure in seasonal 7 hr/day mean ozone concentration (ppm) a = intercept b_0 and b_1 = regression coefficients		
4. (a) Linear yield function $y = b_0 + b_1x$	y = crop yield (g/plant) x = ozone exposure in seasonal 7 hr/day mean ozone concentration (ppm) b_0 = intercept b_1 = slope	Selected crops Range of R^2 = 0.99 to 0.65	Heck et al. (1982)

TABLE 6-28 (cont'd). SUMMARY OF MODELS OF OZONE YIELD AND LOSS

Model	Crop	Reference
(b) Plateau-linear yield function $y = b_0$ if $x \leq f$ $y = (b_0 - b_1 f) + b_1 x$ if $x > f$ y = crop yield (g/plant) x = ozone exposure in seasonal 7 hr/day mean concentration (ppm) f = threshold 7 hr/day mean concentration (ppm) b_0 = intercept b_1 = slope	Range of R^2 = 0.99 to 0.94	
(c) Loss function $y = \frac{100}{a} b_1 (0.025 - x)$ y = % yield reduction b_1 = regression coefficient from function 4(a) a = predicted yield (g/palnt) from function 4(a) at 0.025 ppm 7 hr/day mean ozone concentration x = ozone exposure in seasonal 7 hr/day mean ozone concentration		
5. Weibull function $y = \alpha \exp[-(x/\sigma)^c] + e$ y = yield α = hypothetical maximum yield at 0 ozone x = ozone dose in seasonal 7 hr/day mean ozone concentration (ppm) σ = the ozone concentration when yield is 0.37 α c = dimensionless shape parameter	Selected crops Parameters estimated from empirical data	Heck et al. (1983) Heck et al. (1984a,b)
6. (a) Tuber weight yield function $y = a + bx$ $y = 151[illegible] - 15.8D$ y = % tuber yield (g/plant) D = ozone dose (ppm-hr)	Potato cv Centennial Russet $R^2 = 0.77$	Foster et al. (1983b)
(b) Tuber number yield function $y = 34.3 - 0.318D$ y = tuber yield (number/plant) D = ozone dose (ppm-hr)	$R^2 = 0.62$	
(c) Plant dry matter function $DM = 38[illegible] - [illegible].83D$ DM = total dry matter (g/plant) D = ozone dose (ppm-hr)	$R^2 = 0.73$	

to a predictive loss model using the intercept as the zero-loss reference value. Similar techniques were used to develop an O_3-loss model for fresh market tomatoes (Table 6-28) (Oshima et al., 1977a). This model incorporated the unique feature of transforming plant yield to economic packing container units. Tomato fruit yield was predicted as percentage loss in marketable container units (flats or lugs) based on U.S. Department of Agriculture fruit size categories. The inclusion of the marketing criteria sharply increased the proportion of loss.

Heagle and Heck (1980) developed both linear and quadratic yield models for cultivars of field corn, winter wheat, soybeans, and spinach (Table 6-28). The models were derived from open-top chamber experiments and used a seasonal 7 hr/day mean O_3 concentration to characterize O_3 exposures. These models were the precursors of those developed by NCLAN.

The first published yield models produced by NCLAN (Heck et al., 1982) were presented as either linear or plateau-linear functions (Table 6-28). The plateau-linear function combines two linear functions; the first having a slope of zero, depicting no response, and a second having a measurable slope. The intersection of the two functions can provide an estimate of a threshold value. Yield functions were developed from open-top chamber data obtained by the regional research laboratories participating in the NCLAN program. Each model was developed with a standardized method monitored by a quality-control program. Yield-loss models were developed for cultivars of corn, soybean, kidney bean, head lettuce, peanut, spinach, turnip, and wheat. Some models included in Heck et al. (1982) were generated from earlier experiments that involved the corn, wheat, and spinach models of Heagle et al. (1979a, 1979b, 1979c).

Recently, Heck et al. (1983a, 1984a) used a three-parameter Weibull function to model NCLAN yield losses (Table 6-28). The Weibull function was selected because it has a flexible form that covers the range of observed biological responses; the form of the Weibull is biologically realistic; the model parameters have clear and straightforward interpretations; and it offers a method of summarizing species responses by developing a common proportional model (Rawlings and Cure, 1985). The Weibull modeling approach was subsequently used with NCLAN data previously modeled with linear, plateau-linear, or quadratic functional forms (Heck et al., 1983a).

Larsen and Heck (1984) have recently adapted their lognormal plant injury model (Larsen and Heck, 1976) to estimate the impact of ozone on crop yield. The model uses the "effective mean" O_3 concentration (see Section 6.2.2) to characterize the exposure. The model assumes that equal effective means cause equal impacts and assumes that it does not matter whether the mean is the result of constant or varying ozone concentrations. Similarly, the effects are cumulative with time, which means that the same effects would result from continuous or discontinuous exposures. The exponent on the concentration term for effective mean was derived from injury studies and then applied to yield studies without validation of its applicability to yield. Also, the exponent probably varies with cultivar and environmental conditions. A comparison of the log-normal and Weibull models with the same data set showed that the models produced similar yield reduction curves. In lognormal model did not work well, however, with individual plot means; and the lowest crop reduction value in the data set must be greater than zero with that model because of data transformation needs. The Weibull does not have these same constraints.

Foster et al. (1983a,b) produced yield and plant dry weight functions for Centennial Russet, an extremely sensitive potato cultivar. These models were developed using an ambient exposure facility composed of a series of large Teflon® chambers with O_3 exposure controlled by proportional filtration of ambient O_3.

A multipoint crop-loss technique was developed (by P. Teng, as reported in Benson et al., 1982) and used to assess the impacts of O_3. Previously the multipoint models had been used to predict biotic yield losses (resulting from biotic pathogens) but the authors further refined this technique by summing daily multipoint loss models over a season to arrive at a seasonal loss for alfalfa (Table 6-29). When single harvest crops such as corn, wheat, and potato were used, the authors divided the seasonal exposure into 12 time steps and regressed final harvest on the exposure steps. This application of the model was seriously flawed, however, because only one time series of O_3 exposures was used. Separating total O_3 exposure into several time steps creates a model with several colinear variables. The estimated coefficients of these variables are unstable. The alfalfa model is important because O_3 exposures were represented by multiple variables that indicate specific exposure periods, which may more closely approximate the ambient patterns of exposure than do the single summary statistics used by other researchers.

TABLE 6-29. SUMMARY OF CROP-LOSS MODELS

Model		Loss criteria
General models		
1. $y = f(x_{ti})\ldots$	y = proportion of yield reduction x_i = dose parameter at time t_i	NA[a]
2. Net yield reduction is:	$\sum_{i}^{n} ydt$, where: dt = time step n = maximum number of growing days	NA[a]
Functional models		
1. Alfalfa $y = ax + bx^2 + cx^3$ Range of $R^2 = 0.99$ to 0.13	y = daily yield loss (fresh wt) x = Σ hourly averages for 1 day a to c = regression coefficients	Loss = $1.0 - \frac{\text{Biomass at site } (x)}{\text{Biomass at control site}}$
2. Corn $y = ax_1 + bx_2 \ldots . lx_{12}$ $R^2 = 0.87$	y = yield loss based on 100 kernel wt x_1 to x_{12} = ozone summary statistics for periods 1 to 12 calculated as: $\frac{\sum_{i=1}^{N} [(\Sigma hi/n)24]}{N}$, where: N = the number of days in a period (7 days) hi = ozone concentrations n = number of hours for which there are ozone concentrations a to l = regression coefficients	Loss = $10 - \frac{\text{100 kernel yield for } (x)}{\text{100 kernel yield for control}}$

TABLE 6-29 (cont'd). SUMMARY OF CROP-LOSS MODELS

	Model	Loss criteria
3. Wheat $y = ax_1 + bx_2 \ldots gx_7$ $R^2 = 0.95$	y = yield loss based on 100 seed wt x_1 to x_7 = ozone summary statistics for periods 1 to 7 calculated as: $$\frac{\sum_{i=1}^{N} [(\Sigma hi/n)24]}{N},$$ where: N = the number of days in a period (7) hi = ozone concentrations n = number of hours for which there are ozone concentrations a to g = regression coefficients	$\text{Loss} = 1.0 - \dfrac{\text{100 seed yield for (x)}}{\text{100 seed yield for carbon filtered treatment}}$
4. Potato $y = ax_1 + bx_2 + cx_3 + dx_4 + ex_5$ $R^2 = 0.93$	y = yield loss based on tuber wt/plant x_1 to x_5 = ozone summary statistics for periods 1 to 5 calculated as: $$\frac{\sum_{i=1}^{N} [(\Sigma hi)]}{N},$$ where: N = the number of days in a period (14 days) hi = hourly ozone concentrations in 1 day a to e = regression coefficients	$\text{Loss} = 1.0 - \dfrac{\text{tuber wt yield for (x)}}{\text{tuber wt yield for control treatment}}$

[a] NA = Not available.

Source: Benson et al. (1982).

Three kinds of models have been used to describe yield and loss: linear, plateau-linear, and Weibull functions. These empirical models are intended to describe the behavior of plants in the absence of a known functional relationship between O_3 concentration and yield. Each type of model has strengths and limitations.

The class of linear models, including straight-line and quadratic equations, is very flexible because it can take on a large variety of shapes and can be used to approximate other functions and because statistical methods for computing confidence limits are available (Draper and Smith, 1966). Straight-line models are limited because they allow no curvature and they do not allow threshold levels below which no yield loss occurs. Quadratic models allow curvature and gradual changes in slope, but like straight-line models, they do not allow plateau shapes or thresholds. They can, however, describe situations in which low levels of a pollutant stimulate growth but higher levels cause yield reductions.

Three nonlinear models (plateau-linear, lognormal, and Weibull) have been used in attempts to describe situations in which response to O_3 has a threshold. Statistical theory for nonlinear models is not as well developed as that for linear models and, consequently, confidence bands are not usually fitted to nonlinear models. The plateau-linear model incorporates a threshold value but does not allow curvature of any increase in yield followed by a decrease. The Weibull model can take on a plateau shape followed by curved gradual decreases.

Several types of yield models have been used to describe and ultimately predict expected yield loss from O_3 exposure. This need provides an important constraint for the models; when making predictions it is important that the exposure-response model have more than just a high R^2. The fitted equation should not show systematic deviation from the original data points. Also, the predicted response should not over- or underestimate the response at any particular concentration-duration combinations. Examples of linear and plateau-linear models and their fit to the data are shown in Figures 6-21 and 6-22. Examples of the Weibull curves are shown in Section 6.4.3.2.1.1.

While linear equations were adequate for some cultivars of some crops, nonlinear responses provided a better fit to the data for other crops (Figures 6-21, 6-22). The linear curves for soybean, peanut, and spinach all show good fit to the data and have high R^2. In the case of the soybean (Argonne) and kidney bean data, however, the treatment means show a curvilinear relationship

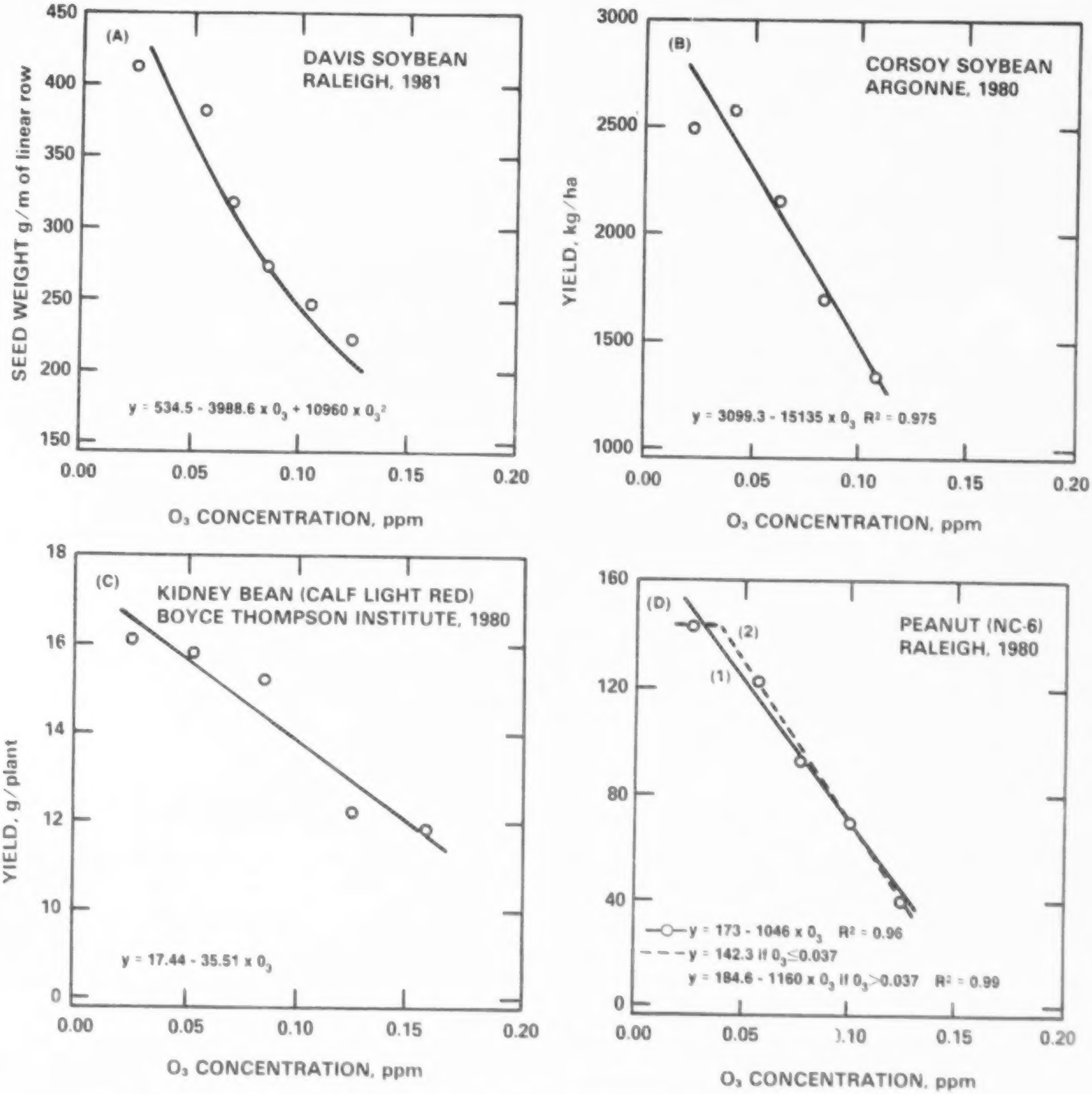

Figure 6-21. Effects of ozone on the yields of several legume species. The O_3 concentration is expressed as the 7-hr seasonal mean. The data were selected to show examples of the goodness of fit of the equations to the data points. (A) Data and regression equation from Heagle et al., (1983a). Each point is the mean of two plots; the regression equation was based on the individual plot values. (B) Data and regression equation are from Kress and Miller, (1983). Data and the curve for yield in g/plant are also given in Heck et al. (1982). Each point is the mean of four plots; the regression equation was based on the individual plot values. (C) Data and regression equation are from Kohut and Laurence (1983). The same data and another straight line regression equation are in Heck et al. (1982). Each point is the mean of three plots; the regression was performed on the treatment means. (D) Data and the straight line equation (1) are found in Heagle et al. (1983b), and Heck et al. (1982); the plateau-linear equation (2) is from Heck et al. (1982).

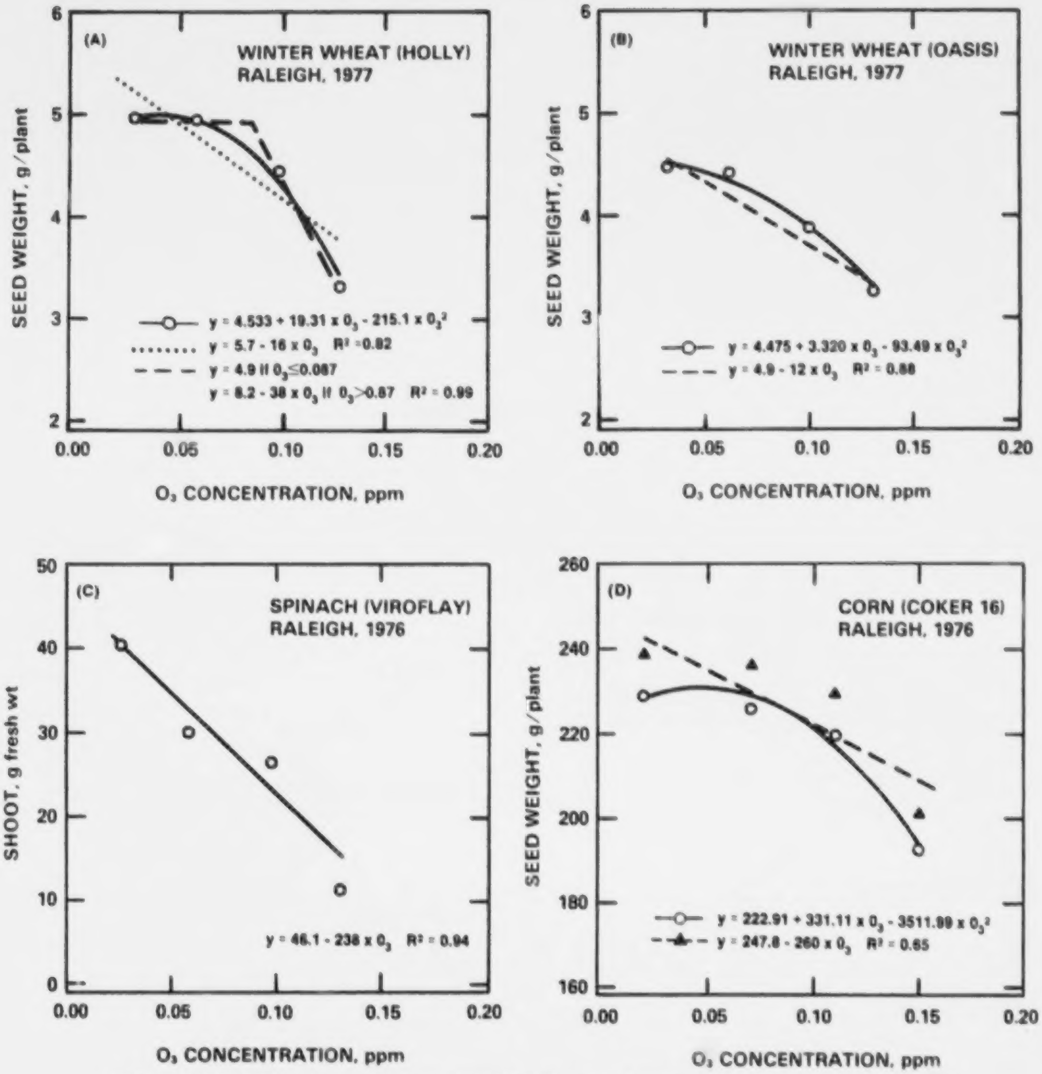

Figure 6-22. Effects of ozone on the yield of several crops. The data were selected to show examples of the goodness of fit of the equations to the data points. The O_3 concentration is expressed as the 7-hr seasonal mean. (A-B) The data are from Heagle et al. (1979c). Quadratic equations are from Heagle and Heck (1980). In Heagle and Heck (1980) the data were presented as the yield per four plants; however, in this figure the values were divided by four to express the yield on a per plant basis. The other equations are from Heck et al. (1982); each point is the mean of four plots with 48 plants per plot. (C) The data are from Heagle et al. (1979b). Regression equations are from Heck et al. (1982). Another set of straight line equations is given in Heagle and Heck (1980). Each point is the mean of four plots with four quadrants (two to three plants per quadrant per plot). (D) Data are from Heagle et al. (1979a) with a correction for the yield at 0.07 ppm (*personal communication from A.S. Heagle, U.S. Dept. of Agriculture, Raleigh, NC, to D.T. Tingey, U.S. EPA, 1984*). The quadratic equation (solid line (○)) is from Heagle and Heck (1980). Data point at the concentration of 0.07 is different from the original paper; the correction was based on information from A.S. Heagle (*personal communication to D.T. Tingey, 1984*). The straight line equation (2) is from Heck et al. (1982). In developing the quadratic equation, the data from Heagle et al. (1979a), were divided by a factor of 1.045 to adjust the moisture content (*personal communication, A.S. Heagle to D.T. Tingey, 1984*); for the linear equation the unadjusted data were used; (▲) indicates an adjusted treatment mean. Each point is the mean of five plots with eight plants/plot.

not well described by the linear regression. With the wheat and corn data the linear provides a poorer fit to the data than curvilinear models. Several nonlinear models would probably fit the data; however, the Weibull was found to fit the data and to have the desirable properties described above. It has been selected as the best of the tested models for fitting most of the NCLAN data (Heck et al., 1983a; Heck et al., 1984b; Rawlings and Cure, 1985).

If the equations do not fit the data well there is a tendency for the model to yield poor predictions. This can be illustrated by calculating the seasonal 7-hr mean O_3 concentration that would be predicted to cause 10 and 30 percent yield reductions (Table 6-30). In every case, the linear model predicted that a substantially lower mean O_3 concentration would cause a 10 percent yield loss than would the Weibull, with the differences ranging from 17 to 57 percent. These differences indicate that great care should be exercised when using only linear models to make yield predictions. The predicted concentrations that would cause 10 percent yield loss were generally similar among the plateau-linear, quadratic, and Weibull models. When exposure-response functions are used to make predictions the user should ensure that the model provides adequate fit to the data.

All the yield and loss models presented have some common weaknesses for production forecasting. With the exception of the model developed by Teng (Benson et al., 1982), none of the models uses a statistic that characterizes the episodic nature of ambient exposures. The multiexposure variables used by Teng (Benson et al., 1982) partition the seasonal exposure into discrete periods. This accounts for some of the ambient fluctuations in O_3 levels. The temporal periods of exposure were preselected, however, and did not correspond to natural fluctuations. Only the alfalfa model incorporated the daily variations in ambient exposures because of the nature of its yield.

6.4.3.3.5 Interpreting exposure-response models. Interpretation of exposure-response models requires an understanding of the subjects presented in Section 6.2. The loss models presented in Tables 6-28 and 6-29 were developed by means of a range of diverse exposure methods, exposure characterizations, experimental designs, and reference loss criteria. Despite their enormous differences, the models are mathematically very similar because all but the Weibull functions used linear or multiple linear regression techniques. All but the Weibull and quadratic models are linear functional forms, use percent as the unit of loss and, with the exception of the model of Teng (see Benson et al., 1982) (Table 6-29), use a single independent variable to represent O_3

TABLE 6-30. COMPARISON OF PREDICTED 7-hr SEASONAL MEAN OZONE CONCENTRATIONS USING VARIOUS YIELD REDUCTION MODELS[a]

Plant	Model	Control O_3 concentration, ppm	Concentration, ppm, for predicted yield loss of: 10%	30%
Soybean				
Corsoy	$kg/ha = 3099.3 - 15135\ O_3$	0.022	0.040	0.077
Corsoy	$g/plant = 15.6 \exp [-(O_3/0.129)^{1.70}]$	0.022	0.043	0.076
Davis	$seed\ wt/m = 534.5 - 3988.6\ O_3 + 10{,}960\ (O_3)^2$	0.025	0.038	0.070
Davis	$g/plant = 31.1 \exp [-(O_3/0.129)^{0.91}]$	0.025	0.038	0.071
Peanut - 1980	$pod\ wt/plant = 173 - 1046\ O_3$	0.025	0.039	0.067
Peanut - 1980	$pod\ wt/plant = 142.3$ if $O_3 \leq 0.037$; $= 184.6 - 1160\ O_3$ if $O_3 > 0.037$	0.025	0.049	0.073
Peanut - 1980	$g/plant = 148 \exp [-(O_3/0.186)^{3.20}]$	0.025	0.046	0.073
Kidney bean	$seed\ wt/plant = 17.44 - 35.51\ O_3$	0.025	0.072	0.165
Kidney bean	$g/plant = 16.5 \exp [-(O_3/0.287)^{1.77}]$	0.025	0.086	0.164
Wheat				
(Holly)	$g/plant = 5.7 - 16\ O_3$	0.03	0.063	0.128
(Holly)	$g/plant = 4.533 + 19.31\ O_3 - 215.1\ (O_3)^2$	0.03	0.095	0.129
(Holly)	$g/plant = 4.95 \exp [-(O_3/0.156)^{4.95}]$	0.03	0.099	0.127
(Holly)	$g/plant = 4.9$ if $x \leq 0.087$ $= 8.2 - 38\ O_3$ if $O_3 > 0.087$	0.03	0.100	0.126

TABLE 6-30 (cont'd). COMPARISONS OF PREDICTED 7-hr SEASONAL MEAN OZONE CONCENTRATIONS USING VARIOUS YIELD REDUCTION MODELS[a]

Plant	Model	Control O_3 concentration, ppm	Concentration, ppm, for predicted yield loss of: 10%	30%
Wheat				
(Oasis)	$g/plant = 4.9 - 12\ O_3$	0.03	0.068	0.143
(Oasis)	$g/plant = 4.475 + 3.320\ O_3 - 93.49\ (O_3)^2$	0.03	0.088	0.138
(Oasis)	$g/plant = 4.88 \exp [-(O_3/0.186)^{3.20}]$	0.03	0.093	0.135
Spinach				
(Viroflay)	$g/plant = 46.1 - 238\ O_3$	0.024	0.041	0.075
(Viroflay)	$g/plant = 41.1 \exp [-(O_3/0.129)^{1.99}]$	0.024	0.048	0.080
Field corn				
(Coker 16)	$g/plant = 247.8 - 260\ O_3$	0.02	0.113	0.300
(Coker 16)	$g/plant = 222.91 + 331.11\ O_3 - 3511.99\ (O_3)^2$	0.02	0.132	---
(Coker 16)	$g/plant = 240 \exp [-(O_3/0.221)^{4.46}]$	0.02	0.133	0.175

[a] The sources for the linear, quadratic, and plateau-linear models are listed in the legends to Figures 6-21 and 6-22; the Weibull curves are from Heck et al. (1983a).

exposure. These models differ because they use several independent variables that represent periods of exposure within a season. For simplicity, these loss models can be represented by a general function:

$$Y = a + b(x) \tag{6-2}$$

Y = yield loss;
a = the regression intercept;
b = regression coefficient; and
x = O_3 exposure representation.

The variable x represents O_3 exposure in the general model. The models presented in Tables 6-28 and 6-29 use different statistics to represent the O_3 exposure, and, as previously stated in Section 6.2.2, these statistics can not be readily transformed for comparison.

The y variable in the general model represents the dependent variable (yield loss). All models utilize percentages as loss units but calculate the loss percentages from different reference zero-loss values. Only a single model (Oshima et al., 1977a) used percentages calculated from commercial marketing criteria. All other models used biological yield parameters as the basis for converting to percentage loss. The models used are the best available, and they serve to define the relationship between O_3 exposure and yield of specific crops. These models also serve as criteria for developing simulation models designed to generate the coefficients necessary to drive the more sophisticated crop production models described by Holt et al. (1979); or serve to focus research in areas required for rational crop-loss assessments (Teng and Oshima, 1982).

Use of a loss model requires O_3 exposure data in the appropriate format, good judgment to guide its application, and an appreciation of what the predicted value represents. The fresh-market tomato loss model (Oshima et al., 1977a) can be used as an example.

$$\text{Loss} = 0.0232\ (O_3 \text{ dose}) \tag{6-3}$$

This linear model predicts the loss in marketing container yield caused by seasonal O_3 exposure expressed as cumulative O_3 dose greater than 0.10 ppm.

This model was developed from ambient plots along an O_3 gradient; therefore, it is representative of plot-level yields. The zero reference level is the intercept of the yield model in Table 6-29.

This model requires a cumulative dose to represent O_3 exposure. Other exposure statistics, such as the seasonal 7-hr daily average used by NCLAN, cannot be used with this model. By calculating the O_3 doses for locations of interest, plot-level predictions can be estimated. The cumulative dose, the exposure statistic used in this model, was derived by summing all 1-hr O_3 concentrations greater than 0.1 ppm for the 7:00 a.m.-to-9:00 p.m. period for each day in the 4-month season.

Examples of loss calculations for three hypothetical locations are:

Location	Ozone dose	Predicted loss
1	500 pphm-hr	11.6%
2	1000 pphm-hr	23.2%
3	1500 pphm-hr	34.8%

The predicted values can be used either to estimate losses in tomato production or to arrive at an estimate of economic crop loss. This distinction must be made because the respective applications of these loss estimates require different procedures. Ideally, the model would include an applications validation test wherein an independent data set of tomato losses at specific O_3 doses would be compared to predicted losses from the model to determine the precision of the estimates.

Once estimates are calculated for locations of interest, the next procedure required is aggregation. The estimates given above represent three plots of plants grown under different O_3 exposure conditions. To represent tomato production on a larger scale, the plot-level estimates must be aggregated to estimate field-level production, the production from all fields in the area, and the production from the region that includes the three fields.

If an economic crop-loss assessment is required, the inputs into the economic model of choice are the estimates or the loss function. The three yield-loss estimates provide the basis for an economic transformation to profit or loss estimates, depending on the factors incorporated into the economic model. For instance, if they are inputs into the linear-program, representative-farm model used by NCLAN, then grower crop substitutions, alternate cultural practices, and other farm-level options would be explored to determine predicted economic impact. The aggregation methods would be economically derived and would probably incorporate regional supply and demand, market price dynamics, and regional linkages. Alternative approaches such as econometric modeling might be selected in some instances.

Use of a yield-loss model is a process that requires adhering to the limitations and requirements of the model, having the required data necessary to drive the model, deciding on the specific application desired, and using the appropriate step to aggregate estimates to the organizational level required.

6.5 ECONOMIC ASSESSMENTS OF EFFECTS OF OZONE ON AGRICULTURE

Previous sections of this chapter discuss the adverse effects of ozone on crop productivity. Evidence from the plant science literature clearly demonstrates that ozone at ambient levels will reduce yields of some crops (see Section 6.4.3.2.2, Biomass and Yield Responses from Ambient Exposures). In view of the importance of U.S. agriculture to both domestic and world consumption of food and fiber, such reductions in crop yields as a result of exposure to O_3 could adversely affect human welfare. The plausibility of this premise has resulted in numerous attempts to assess, in monetary terms, the losses from ambient O_3 or the benefits of O_3 control. Many of these assessments have been performed since the 1978 ozone criteria document was published (U.S. Environmental Protection Agency, 1978). The methodologies and resulting estimates from these post-1978 studies, and their validity with respect to plant science data and economic theory, are discussed in this section. Specifically, a set of biological, aerometric, and economic criteria important to the validity of such assessments will be presented. Post-1978 assessments purporting to estimate the economic effects of O_3 on agricultural production will then be evaluated in terms of how well the assessments deal with these biological and economic criteria. The section will also draw conclusions concerning the likely magnitude of national-level economic effects of O_3 reductions suggested by two recent studies that have strong plant science and economic foundations relative to any previous research.

6.5.1 Economic Issues in Performing Assessments

Decision-making related to the formation of public policy centers on perceived changes in "public welfare." In a benefit-cost analysis of ambient air quality changes, however, regulatory actions typically do not lead to a regulation from which all parties benefit. Virtually any air pollution control action or regulation will disadvantage someone (e.g., polluters, consumers, agricultural producers) in terms of perceived welfare. Thus, in evaluating a given policy, a quantifiable measure of social welfare across all parties is needed as a basis for judging socially desirable changes associated with alternative pollution control actions. This also implies the need for consistent measures of value for the various components of public welfare, e.g., the welfare of producers, consumers, and input suppliers, so that distributional effects can be evaluated.

The theoretically consistent measures of economic welfare are "compensating or equivalent variation." These somewhat abstract theoretical concepts define welfare changes in terms of income equivalents as captured in the "willingness to pay" or "willingness to accept compensation" by individuals for alternative economic or environmental states. In practice, these concepts are calculated as consumers' and producers' surpluses, defined as the geometric (and hence measurable) area between the supply and demand curves and to the left of their intersection (see Just et al., 1982, or Willig, 1976, for definitions and more extensive discussions of the validity of this triangular area as a measure of welfare). Consumers' and producers' surpluses approximate the utility gained by individuals when: (1) in consuming goods, they obtain goods at a price less than the maximum they would be willing to pay; and (2) in producing goods, they sell at a price above the price at which they would have been willing to supply. Most economic assessments of environmental change or other policy options measure benefits in terms of changes in economic surplus (the sum of consumers' and producers' surpluses) associated with supply and price adjustments resulting from the environmental change. When the net change in total economic surplus arising from a given policy or standard is positive, then that policy may be viewed as beneficial (ignoring distributional aspects).

While economic surplus is an accepted measure of aggregate welfare, the distribution of impacts across and within the consumer and producer categories is another dimension of welfare. Several distributional issues that arise then in an assessment of air pollution policies include:

1. How are gains or losses, or both, distributed between various classes of people (e.g., tradeoffs between consumers and producers)?
2. How are gains or losses, or both, distributed with respect to geographical region or commodity, or among the owners of factors of production?
3. How are gains or losses, or both, distributed within a class of people (e.g., tradeoffs among consumers at different income levels, or among producers with different farm sizes and endowments)?
4. How do the distributional effects change with time?

The latter two distributional concerns are currently difficult to address because of insufficient data. The first two, however, can be measured directly by capturing appropriate supply, demand, and resource relationships within the economic analysis. Failure to include these relationships will result in misleading estimates whenever: (1) prices in the markets for agricultural inputs or outputs are sensitive to changes in yield and input usage as the result of changes in air quality; and (2) producers and consumers adopt different ways of adjusting to changes in air quality. In the first instance, consider the case in which improvements in air quality result in yield increases, but in which these improvements in turn cause price reductions. If the price reductions are greater than the yield increases, producers could actually be worse off than before the air quality improvement. An assessment that ignored such price effects would then wrongly attribute benefits as accruing to the producer when in reality the producer sustained revenue losses (and the consumer, gains).

The second issue, with respect to producer and consumer adaptation strategies, relates to the nature of the affected individual's resource, technical, income, and environmental endowments. Specifically, the decision options that underlie an individual's response to a given environmental or policy change need to be identified and modeled. For example, producers can reduce their potential losses or increase their gains from an air pollution change by adopting different production patterns, utilizing more resistant cultivars, or adding fertilizer or other compensating inputs. Failure to account for this adaptive producer behavior will result in overestimates of losses experienced by producers in the face of air quality degradation. Similarly, consumers may substitute certain agricultural commodities in the face of relative price changes, so that the net effect of a rise in the price of a commodity as the result of air pollution-induced supply changes may not be as severe as first indicated. The implication of this discussion is that a properly formulated assessment should capture the relevant behavior of economic agents, which will then lead to more accurate predictions of agricultural supply changes associated with O_3 changes. This will help ensure that the estimates of economic well-being (consumers' and producers' surpluses) are valid indicators of the benefits or costs of changes in air quality.

6.5.2 Plant Science and Aerometric Issues in Performing Economic Assessments

In addition to the correct modeling of economic responses, assessments of damage to agricultural or other ecosystems from pollution require specific plant science data linking pollutant levels and performance parameters of the ecosystem in question. For agriculture, this information is represented by a relationship between the response (changes) in crop yield and changes in pollutant concentration or dose levels and other causal factors. The relationship may be quantified directly using data generated from biological experimentation, indirectly from observed producer data (actual input and yield data from a large sample of individual producers), or from some combination of data sources. From the standpoint of direct applicability to economic assessments, estimates that are based on observed producer data are preferred. While some success has been achieved in capturing the relationship between yields and O_3 by applying procedures based on producer input and yield data over relatively homogeneous areas (e.g., see Mjelde et al., 1984), assessors in general have had little success in directly applying such techniques across large geographical areas, because of both data and statistical difficulties (e.g., see Adams et al., 1982; Manuel et al., 1981). Even for those studies in which plausible biological estimates are used, related experimental data are required initially to formulate testable hypotheses about yields and O_3 levels as well as to establish the credibility of estimates derived from producer data. As a result, assessments of pollutant damages to agriculture rely heavily on data from some form of biological experimentation to define the relationship between dose and plant response.

To be of use to the economist, the form of these experimental data on yield and pollution levels must be minimally compatible with the nature of economic markets. This was explicitly recognized in the 1978 criteria document

(U.S. Environmental Protection Agency, 1978) and in Section 6.2.5 of this chapter, where a distinction was made between injury (defined as any identifiable and measurable response of a plant to air pollution) and loss (defined as any measurable adverse effect on the desired or intended use of the plant). Such a distinction is made because the evaluation of the economic effects of O_3 exposure requires that the plant be altered either quantitatively (yield) or qualitatively (market acceptability) so as to change its value. In some cases exposure may result in injury, such as leaf necrosis, without affecting yield. In addition to the need to focus on crop yield response, the closer the experimental procedures are to commercial production conditions, the more likely the responses are to mimic actual producer yield changes; and, hence, the more useful they are in economic assessments.

The need for plant response information measured in terms of yield units (rather than foliar injury) consistent with field conditions has been noted by most analysts doing assessment research (e.g., Leung et al., 1978; Adams and Crocker, 1982). Plant scientists have also recognized the need to report response in terms of yield if economic losses are eventually to be estimated. For example, Oshima and coworkers (Oshima, 1973; Oshima et al., 1976; Oshima and Gallavan, 1980) reported crop losses in terms of potential or actual yield reduction for selected crops. More recently, the NCLAN program (see, e.g., Heck et al.; 1983a,b; 1982) appears to be the first coordinated plant science research effort intended to provide response information in a usable form for economic assessments. The nature of the NCLAN protocols and results are discussed in Section 6.4.3.2.2. As evidence of the utility of this and similar efforts, NCLAN response data have been used to derive most of the economic estimates reported in this chapter.

Prior to the availability of NCLAN data, researchers needing yield-response data have either extrapolated from a narrow and often incomplete set of existing O_3 response functions reported in the plant science literature; or have estimated these relationships from secondary data on production and air quality, with attendant statistical and measurement problems. The credibility of these extrapolation or estimation procedures and their implications in terms of the resultant yield loss estimates are questionable, given that the estimated yield responses diverge sharply in most cases from the replicable NCLAN results. As a result, the plant science data used in earlier economic assessments, along with misspecified or overly simplified economic models, must be recognized as a potentially critical source of uncertainty in resulting crop loss estimates.

The air quality data used in assessments are also critical inputs. Specifically, the yield changes predicted by the response functions are driven by assumed changes in O_3 exposure, typically measured by the difference between actual and anticipated O_3 levels for the region in question. Estimating current ambient levels of O_3 or linking changes in SNAAQS (Secondary National Ambient Air Quality Standard) to actual rural concentrations presents difficult analytical and data problems. Calculating current ambient concentrations is difficult because few monitoring sites exist in rural areas, where the bulk of agricultural crops are grown. The complex meteorology of O_3 formation and transport also makes difficult the development of models for defining changes in rural concentrations resulting from changes in urban emissions. Errors in either estimation will lead to biases in the predicted yield changes used in any assessment. The latter issue can be circumvented by developing air quality scenarios based on hypothetical changes in rural concentration (e.g., percentage reductions from actual), rather than on specific changes in SNAAQS; but this limits the usefulness of the assessment in formulating policy. Even with such an assumption, there is still a need to have actual or estimated ambient concentrations as a base from which to develop and compare hypothetical O_3 changes.

The effects of plant science and aerometric assumptions and extrapolations on monetary estimates are reflected in the highly divergent loss estimates reported for O_3 in the 1978 document. The divergences in the pre-1978 assessments, as well as those in some of the assessments to be reviewed subsequently, may be partially attributable to the following summary list of plant science and air quality data problems:

1. The effect of sparse data on O_3-induced crop losses. A lack of data caused past assessments to be based on extrapolations from available foliar injury estimates, resulting in often unreliable yield-reduction estimates.
2. Selection of alternative cultivar and crop mixes, regions, and time periods in the analysis. Crop prices, production levels, and O_3 exposure vary geographically and temporally, with resultant changes in dollar loss estimates.
3. Selection or definition of alternative background ambient levels to portray "clean air" (absence of anthropogenic O_3) in the analysis.

When used in combination with a standardized dose-response function, the use of different background ozone levels results in different yield reduction estimates and, ultimately, different monetary estimates.

4. The difficulty of extrapolating from controlled-chamber experiments to agronomic regions with all the required assumptions regarding soil type, precipitation regimes, O_3 exposure patterns, solar radiation levels, and interactions among these edaphic and climatic variables.
5. The use of different measures of "dose" or exposure. For example, in the recent NCLAN experiments dose was standardized as the seasonal 7-hour average in ppm. Other researchers use cumulative dose (e.g., hours of exposure to levels exceeding 0.10 ppm) or some other measure. Establishing the meteorological linkage between these various dose measures and secondary standards, as well as their correspondence to levels of exposure actually realized by the plant, is an important research area.

The uncertainties associated with some of these plant science and aerometric issues have been partially resolved in more recent assessments by the availability of standardized NCLAN data, as discussed subsequently. While the post-1978 assessments feature a more uniform set of plant science and aerometric data, a range of assessment techniques have been employed in generating the economic estimates. It is not possible to sort out the relative contribution of economic data and assumptions vis-a-vis that of plant science and aerometric data to the accuracy of past assessments without doing the assessments over. Recent empirical work by Adams et al. (1982) suggests, however, that economic and biological processes contribute equally to the measurement of net benefits. The implication of this observation is that an accurate portrayal of both plant science and economic responses is important in performing economic assessments. Studies lacking in either category should be viewed as incomplete analyses. In the following review, both the plant science and economic foundations of recent assessments are evaluated.

6.5.3 Assessment Methodologies Applied to Agriculture

Assessments of air pollution damages to agriculture found in the literature fall within three broad methodological categories: damage function-crop loss models, simple monetary calculation procedures, and economic assessment methodologies. While all three benefit from the use of defensible plant science and aerometric data, only the latter category is capable of portraying the above economic mechanisms that underlie the actual costs or benefits of pollution changes.

The first type of assessment uses predictions of yield changes from damage or response functions to estimate crop losses in physical units, such as the reduction in actual or potential crop production in a given geographical unit (e.g., a state or region). Examples include the assessments by Loucks and Armentano (1982) and Moskowitz et al. (1982). While this approach fails to incorporate the producer responses that determine the net supply effect of the initial O_3-induced yield changes, the authors of these assessments make no claim of having reported economic losses and thus these assessments are not reviewed in this document.

The second, or "traditional" procedure, that is, traditional in the sense that most assessments of air pollution prior to 1982 calculated dollar estimates in this fashion, is a commonly used approach for calculating the dollar or monetary effects of environmental change. In this type of assessment, increases or decreases in production calculated from damage functions are translated into a dollar value by multiplying the predicted yield or production changes by an assumed constant crop price. The advantage of such a procedure is the relative ease with which dollar values may be obtained, since the only economic information required to perform the calculation is the price (usually last season's average price) of the crop in question. As an assessment methodology for obtaining accurate economic estimates, however, it suffers from serious conceptual weaknesses by failing to recognize and account for the complex processes underlying economic response discussed in Section 6.5.1. This limits the validity of the estimates to some very restrictive cases. Thus, while economic theory assumes that value can be expressed in monetary terms, not all dollar loss estimates (including those obtained by the traditional, monetary approach) should be viewed as valid economic estimates.

The third type of assessment framework features the use of standard economic methodologies that address some of the economic issues raised in the preceding section. As such, the procedures within this category are capable of providing estimates of the benefits of air pollution control in dollar terms that account for producer-consumer decision-making processes, associated market adjustments, and perhaps some measure of the distributional consequences of alternative environmental policies or actions. Examples include the economic assessments reported in Leung et al. (1982), Benson et al. (1982), Adams et al. (1982), Mjelde et al. (1984), Kopp et al. (1984), or Adams et al. (1984b), in which attempts have been made to include the market impacts of air pollution-induced yield reductions and producer responses. While they involve somewhat different analytical (solution) procedures as determined by the structure of the particular economic problem, these studies all explicitly deal with price adjustments, providing estimates of the economic effects on producers and consumers. A detailed review of alternative economic techniques and their suitability in assessing various environmental changes or policies is presented in Freeman (1979).

Although economists discount the monetary estimates obtained from the traditional "price times quantity" type of assessments (e.g., critiques of this approach may be found in Just et al., 1982, and Crocker, 1982), estimates arising from traditional and economic assessment methodologies are seldom distinguished in the popular press. Failure to distinguish between the nature of the methodologies has important policy implications in that the estimates from the traditional procedure may be badly biased, leading to potentially incorrect policy decisions. For example, assessments obtained from comprehensive economic analyses have been compared with estimates obtained from the traditional procedure using the same data (see Benson et al., 1982, and Adams et al., 1982). The differences were moderate to large, with the traditional procedure overestimating the costs of air pollution when a "clean air" and ambient ozone condition (an environmental degradation) were compared. Also, the traditional procedure provides estimates that address only producers' effects with no attention paid to the impact on consumers. In some agricultural situations, it is possible that this naive approach will predict producer losses when in fact there are potential gains. Thus, there are fundamental conceptual and empirical differences between monetary estimates calculated by the traditional procedure and those obtained from more defensible economic assessments.

6.5.4 Review of Economic Assessments of Effects of Ozone on Agriculture

Both regional and national assessments are found in the post-1978 literature. While each can provide useful information, the geographical scale in an assessment has implications for the validity and tractability of alternative assessment techniques. For this reason, regional and national studies are discussed separately. Only the third type of assessment framework that was discussed in the previous section, featuring techniques that are capable of addressing economic responses, is included in the regional review. In the review of studies at the national level, assessments based on both the simple "price times quantity" and economic approaches are discussed. Estimates from both types are presented because of the importance normally attached to any national estimate of pollution damage by the popular press and the resultant need to make explicit any limitations inherent in the underlying analyses. The emphasis of this discussion is on how well the assessments conform to economic realities as defined in Section 6.5.1. As noted in Section 6.5.2, however, the plant science and aerometric data are critical inputs in these studies. These data are defined in detail for each study.

6.5.4.1 Review of Regional Assessments. Most of the economic assessments in the literature focus on O_3 effects in specific regions, primarily California and the Corn Belt (Illinois, Indiana, Iowa, Ohio, and Missouri). This regional emphasis may be attributed to the relative abundance of data on crop response and air quality for selected regions, as well as the national importance of these agricultural regions. While regional estimates are not usually sufficient for measuring the national implications of alternative SNAAQS, such studies can provide estimates of the benefits of regional O_3 changes, and hence of state or regional compliance, as well as useful comparative information on alternative economic methodologies for assessing environmental damages. Also, regional estimates may be indicative of the potential magnitudes of national effects for certain crops, if that region produces a dominant share of those crops.

Economic estimates of pollution effects for selected regions are presented in Table 6-31. In addition to reporting the actual monetary loss or benefit estimates derived from each assessment, the table contains considerable detail on the critical plant science, aerometric and economic data, and assumptions used in each assessment. The estimates can then be evaluated relative to the nature of these data and assumptions.

Four of the regional studies have focused on California, a state with both high O_3 levels and an important agricultural economy. Adams et al. (1982) assessed the impact of O_3 on 14 annual vegetable and field crops in

TABLE 6-31. SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study/ region	Crops and no. of cultivars	Annual benefits of control ($ million)	Evaluation of critical data and assumptions			Additional comments
			Plant response data	Aerometric data	Economic model/data	
Adams et al. (1982); Southern California	12 annual crops: beans, broccoli, cantaloupes, carrots, cauliflower, celery, lettuce, onions, potatoes, tomatoes, cotton, and sugar beets. No cultivar-specific responses.	$45 (in 1976 dollars)	Larsen-Heck (1976) foliar injury models converted to yield losses for all crops excluding tomatoes. Tomatoes derived from yield response function by Oshima et al. (1977a).	California Air Resources Board hourly data collected for sites closest to production regions defined in the economic model. Exposure measured as cumulative seasonal exposure in excess of California standard (0.08 ppm)	A price endogenous mathematical (quadratic) programming model reflecting agronomic, environmental, and economic conditions in 1976. Base cost, yield, and input data derived from university, state, and Federal sources.	Economic effects measured as a change in economic surplus (sum of consumers' and producers' surpluses) between base case (actual O_3 levels in 1976) and economic surplus that would be realized if all regions were in compliance with 1976 standard of 0.08 ppm.
Leung et al. (1982); Southern California	9 crops: lemons, oranges (Valencia and Navel), strawberries, tomatoes, alfalfa, avocados, lettuce, and celery. Results estimated across all cultivars contained in county-average yields (see "Plant response data" column).	$103 (in 1975 dollars)	O_3 yield response functions estimated from secondary data on crop yields (county-level averages), regressed on agronomic and environmental variables, including ambient O_3 levels.	Exposure measured in average monthly concentration in ppm for 12-hr period (7:00 a.m. to 7:00 p.m.) Data from 61 California Air Resources Board monitoring sites.	Economic model is composed of linear supply and demand curves for each crop, estimated with data from 1958 to 1977.	Economic effect is measured as a change in economic surplus between base case (1975) and a clean air environment reflecting zero O_3.
Howitt et al. (1984a,b); California	13 crops: alfalfa, barley, beans, celery, corn, cotton, grain sorghum, lettuce, onions, potatoes, rice, tomatoes, and wheat. One cultivar of each crop.	From $35 (benefit of control to 0.04 ppm) to $157 (loss for increase to 0.08 ppm) (in 1978 dollars).	O_3 yield response functions derived from NCLAN data through 1982. Both quadratic and Weibull functional forms used. Alfalfa response from Oshima et al. (1976). Response data available for only 10 crops; for celery, onions, rice, and potatoes, surrogate responses used.	California Air Resources Board data for monitoring sites closest to rural production areas. Exposure measured as the seasonal 7-hr average in each production area for compatibility with NCLAN exposure.	Economic model similar to Adams et al. (1982) but includes some perennial crops and reflects 1978 economic and technical environment.	Economic effects measured as changes in economic surplus across three O_3 changes from 1978 actual levels. These include changes in ambient O_3 to 0.04, 0.05, and 0.08 ppm across all regions.

TABLE 6-31 (cont'd). SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study/ region	Crops and no. of cultivars	Annual benefits of control ($ million)	Evaluation of critical data and assumptions: Plant response data	Evaluation of critical data and assumptions: Aerometric data	Evaluation of critical data and assumptions: Economic model/data	Additional comments
Rowe et al. (1984); San Joaquin Valley in California	14 annual and perennial crops: alfalfa, barley, beans, carrots, corn, cotton, grain sorghum, grass hay, grapes, pasture, potatoes, safflower, tomatoes, and wheat. One cultivar for some crops; others estimated across all cultivars, as contained in county-average yields (see "Plant response data" column.	$43 to $117 depending on degree of control (measured in 1978 dollars).	Response functions based on both experimental data and secondary data. Lettuce, tomato, corn, wheat, and grain sorghum data from NCLAN. Alfalfa from Brewer and Ashcroft (1982). Response functions for beans, cotton, and grapes from regression of county yields on economic and environmental variables. Responses for the remaining crops were based on surrogate responses of similar crops in the data set.	4 exposure levels were tested: range from average 1-hr concentration to a cumulative dose where O_3 $\geq$0.10 ppm. Each dose was measured over an 8-hr period (9:00 a.m. to 5:00 p.m.) and was tested in the estimated response function for each crop. The average hourly concentration was used in most functions to predict changes. All data were from California Air Resources Board monitoring sites in predominantly rural areas.	Same as Howitt et al. (1984a,b).	Economic effects measured as the change in economic surplus between the 1978 base case and three increasingly stringent control scenarios: (1) a 50% reduction in number of hr $\geq$0.10 ppm; (2) meeting the current California standard of 0.10 ppm; and (3) meeting an O_3 standard of 0.08 ppm.
Page et al. (1982); Ohio River Basin	3 crops: corn, soybeans, and wheat. Several cultivars of corn and soybeans may be reflected in the biological data used by Loucks and Armentano (1982) (see "Plant response data" column).	$7,022 (measured in 1976 dollars). This is present value of producer losses for period 1976 to 2000. Annualized losses are approx. $270 in 1976 dollars.	Crop losses provided by Loucks and Armentano (1982) as part of ORBES project. Yield responses derived by synthesis of existing experimental data (from sites outside the Ohio River Basin). These response functions then used to predict changes in total crop production in Ohio River Basin between production under "clean air" (defined as a background of of 0.03 ppm for O_3) and production under a range of energy use scenarios.	Dose measured as cumulative seasonal exposure for a 7-hr period (9:30 a.m. to 4:30 p.m.) for 1977. Monitoring sites at 4 locations were used to characterize the regional exposure.	The economic model consists of regional supply curves for each of the 3 crops. The predicted changes in production between "clean air" case and each scenario are used to shift crop supply curves. Losses represent present value of losses for the period 1976-2000, discounted at 10%. The analysis ignores price changes from shifts in supply.	Losses are measured as differences in producer surplus across the various scenarios. Since prices are assumed fixed (in real terms) over the period, no consumer effects are measured.

TABLE 6-31 (cont'd). SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study/ region	Crops and no. of cultivars	Annual benefits of control ($ million)	Evaluation of critical data and assumptions			Additional comments
			Plant response data	Aerometric data	Economic model/data	
Benson et al. (1982); Minnesota	4 crops: alfalfa, wheat, corn, and potatoes. Cultivars limited to one per crop.	$30.5 (measured in 1980 dollars).	Like the Loucks and Armentano (1982) study, O_3-response functions based on crop loss models estimated using experimental O_3-yield data from other researchers (from sites outside Minnesota). Crop loss modeling includes both chronic and episodic response and crop development stage as factors in yield response, by regressing yield on O_3 expousres for various time windows during the growing season. Several functional forms used to test relationships between yield and dose. Yield losses for several O_3 scenarios were measured against production under a zero background. O_3 scenarios represent increases in both concentrations and frequency of occurrence.	Air quality data are for state of Minnesota for 1979 and 1980. Exposure measured several ways but generally as a daily exposure statistic reflecting either sum of hourly averages or the mean hourly average. These exposures were then summed over various time invervals to represent the exposure for the various periods indicated in the seasonal crop loss models.	The economic estimates are derived from a comprehensive economic model of the U.S. agricultural sector that includes equations capturing crop supply and demand across multiple domestic and foreign markets. Model is calibrated to 1980 values.	The economic effect for each O_3 scenario measured in terms of short-run profit changes for Minnesota producers under 2 regional assumptions. In the first case, yields are assumed to change only in Minnesota. In the second case, yields change in Minnesota and the rest of the U.S. In the first case, losses to Minnesota producers are $30.5 million for the most extreme O_3 increase. In the second, producers gain $67 million as a result of increases in crop prices when the yields for all the U.S. are reduced.
Adams and McCarl (1985); Corn Belt	3 crops: corn, soybeans, and wheat. Five cultivars of soybeans, 3 of wheat, and 2 of corn.	$668 (in 1980 dollars).	O_3-yield response information from NCLAN for 3 years (1980-1982). Yield adjustments estimated from Weibull response models.	Air quality data for the growing season are interpolated from SAROAD monitoring sites by Kriging procedure.[a] Represents rural concentration for 1980. Exposure is measured as seasonal 7-hr average to be compatible with NCLAN exposures.	Economic estimates are generated by a mathematical programming model of U.S. agriculture reflecting 1980 supply, demand, and input characteristics. Farm level response is portrayed by 12 individual "representative" farm models that are used to generate supply adjustments used in the national level model.	Economic estimates represent changes in economic surplus (sum of consumers' and producers' surpluses) between current (1980) O_3 levels and increases and decreases in ambient O_3 levels. Reduction to a uniform ambient level of 0.04 ppm across all regions results in benefits of $668 million.

TABLE 6-31 (cont'd). SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study/ region	Crops and no. of cultivars	Annual benefits of control ($ million)	Evaluation of critical data and assumptions: Plant response data	Aerometric data	Economic model/data	Additional comments
Mjelde et al. (1984); Illinois	3 crops: corn, soybeans, and wheat. Responses represent mix of all cultivars actually grown by farmers in the study.	Ranges from $55 to $220 annually for period 1976 to 1980.	Responses are estimated from secondary (non-experimental) data on actual farmer yield, input, and O_3 concentrations. The procedure is conceptually similar to methods used earlier by Adams et al. (1982) and Leung et al. (1982) except that relationship being modeled is the effect of O_3 on farmer profit, rather than yield. Results are translated into yield effects and compared to NCLAN data from Illinois (Argonne National Laboratory).	Same Kriged data set as used in Adams and McCarl (1985),but for Illinois only and covering 5 yr (1976-1980). Exposure is measured as seasonal 7-hr average to facilitate comparison with NCLAN response estimates.	Economic model consists of a series of annual relationships on farmers' profits (profit functions). These functions are adjusted to represent changes in O_3 (±25%) for each year. Model does not include consumer (demand) effects.	The estimates represent increases in farmers' profits that could arise for a 25% reduction in O_3 for each year (1976-1980). Years with higher ambient levels of O_3 have highest potential increase in profits for changes. No effects on consumers estimated.

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[a] Kriging is a spatial interpolation procedure that has been used to generate O_3 concentration data for rural areas in which no monitoring sites have been established. See Heck et al. (1983b).

four agricultural subregions of central and southern California for 1976 using a mathematical programming model of the California agricultural economy. (Mathematical programming is an analytical technique for maximizing or minimizing an objective function equation subject to a set of constraint equations. The equations in such a problem, however, can be given a specific economic interpretation consistent with the behavior of individual producers or consumers, such as maximizing profit or economic surplus, or minimizing costs) (Adams et al., 1982). The economic model captures price changes through inclusion of linear demand relationships for each crop. To establish its general accuracy, the model was calibrated against 1976 production data. The model was then used to predict the effects of changed O_3 levels on crop price, output, and the resultant impact on the welfare of both producers and consumers as measured by changes in consumers' and producers' surpluses.

In view of the sparse experimental data available at the time, the authors initially attempted to estimate O_3-yield relationships from regression procedures based on secondary data (county average yields regressed on O_3 levels and other inputs measured over a 20-year period). The estimation results, however, were mixed, with some variables showing implausible signs and many statistically insignificant coefficients. As a result, O_3-induced reductions in yield were estimated for most crops from the Larsen-Heck foliar injury models (Larsen and Heck, 1976; Larsen et al., 1983). Foliar injury, as predicted by the Larsen-Heck models, was then converted to yield loss using Millecan's "rule of thumb" (1971). The Oshima et al. model (1976) was used for tomatoes. These projected yield changes are at best approximations, given the tenuous link between foliar injury and crop yield. The response functions were used to predict yield changes between actual O_3 levels and levels that would be realized if the state standard had been met. Data from the California Air Resources Board were used for ambient 1976 O_3 levels. Using the predicted yield changes, crop production, price, and economic surplus were estimated as if the standard of 0.08 ppm, not to be exceeded more than one day per year, had been achieved. The increase in economic surplus between the base economic surplus and that under the lower O_3 level is the benefit of control.

As a percentage of total crop value (about $1.5 billion), estimated losses attributable to air pollution were found to be small, $45.2 million. In terms of distributional consequences, meeting the 1976 standard would have increased 1976 agricultural income (producer surplus) by $35.1 million and consumers' welfare (ordinary consumer surplus) by $10.1 million. To provide a comparison, the authors also applied the traditional method of computing losses (multiplying the estimated difference between actual and potential yield by market price) and obtained a total estimated loss of $52.5 million. While the difference in estimates between the methods appears small, the traditional procedure measures only the effects on producers. Thus, if this latter figure ($52.5 million) is compared with the producer loss from the economic analysis ($35.1 million), the difference is approximately a 50-percent greater loss estimate when the traditional approach is used.

Leung et al. (1982) estimated O_3 damage to nine annual and perennial crops in the California South Coast Air Basin, representing about 40 percent of crop production value in the region. Ozone-yield relationships were derived from regression procedures applied to secondary data, rather than from experimental data. Crop yields for 1963 through 1975 were obtained from reports from county agricultural commissioners on yields realized by farmers. Principal component analysis (PCA), a technique in which highly correlated variables are replaced with one or two components that contain most of the information of the original variables, was used to transform monthly environmental data, such as O_3 concentration, temperature, relative humidity, and precipitation, into yearly indices. Then yield was regressed on these indices using linear regression procedures. Finally, crop-yield changes were estimated for 1975 by calculating differences between actual yields (with 1975 levels of O_3) and yields predicted at a zero O_3 concentration.

Leung et al. (1982) then calculated changes in consumer and producer surpluses measured from an economic model containing linear supply and demand relationships to approximate the welfare effects of changes in agricultural supply brought about by air pollution. Specifically, the predicted yield changes were used to shift the crop supply curves, thus generating a new level of economic surplus. Estimated 1976 losses of consumer and producer surpluses from O_3 exposure were $103 million.

The estimate of direct economic loss was subjected to input-output analysis, which traces the economy-wide effects of changes in a single economic variable, to determine the indirect impact to related economic sectors in California. Leung et al. (1982) estimated the indirect loss of sales from O_3 damage to be $276 million in the study region and $36.6 million in the rest of the state. These figures translate into lost income of $117 million attributable to air pollution in the region and $14.1 million in the rest of state.

While the Leung et al. (1982) analysis represents a worthwhile attempt to overcome some data and statistical problems that have plagued economic assessments of pollution damage, a number of limitations need to be recognized. First, by assuming a zero background O_3 concentration, the economic losses from manmade O_3 are overstated if the true background O_3 (including biogenic contributions) level exceeds zero. While the actual background O_3 level is still at issue in the literature, some researchers suggest a minimum background level of 0.025 ppm, measured as a seasonal 7-hr average (Heck et al., 1984a,b). Since the ambient seasonal 7-hr averages for major production regions in California tend to be about twice this value, the Leung et al. (1982) yield losses may be overstated by a factor of two (assuming a linear response function). Second, the use of principal components for O_3, while perhaps reducing multicollinearity, introduces some additional statistical problems, such as whether the variability in the principal component for O_3 bears any resemblance to how crop yields may actually change. Further, it is difficult to interpret the principal component indices in terms of actual policy (O_3) changes. Finally, given the national linkages involved in California agriculture, the use of a regional input-output model for agriculture may be overstating the magnitude of the multipliers used to link primary or direct effects to secondary economic effects. Inflated multipliers will then inflate the regional economic effects. An additional caveat should be noted in reporting economic surplus changes along with other income effects, such as from an input-output model, because the economic surplus changes, if measured in a final market, may already account for some of the welfare changes in input markets. Thus, the income losses from the input-output model should not be aggregated with the economic surplus estimate.

Two more recent studies have also examined the effects of air pollutants (primarily O_3) on California agriculture. In the first, Howitt et al. (1984a) assessed the impact of alternative O_3 levels on the statewide production of fourteen annual crops. The economic model used was similar to that employed in Adams et al. (1982); i.e., a price-endogenous mathematical programming model, scaled to 1978 values. The yield response data were derived from NCLAN experiments through 1982, with the exception of those for alfalfa, which were taken from Oshima et al. (1976).

Howitt et al. (1984a,b) examined three O_3 scenarios, reflecting hypothetical changes in ambient O_3 levels to 0.04, 0.05, and 0.08 ppm seasonal 7-hr averages for nine production areas in California. The first (0.04 ppm) was a reduction of approximately 25 percent in ambient ozone from actual 1978 values across the production regions in the model, where the 1978 O_3 levels were derived from California Air Resources Board data, converted to seasonal 7-hr averages. The second portrayed a slight degradation in air quality (increase in ozone) from actual levels. The 0.08 ppm analysis portrayed an increase of about 60 percent in ambient O_3 for the same regions. The economic effects of meeting the two extreme O_3 actions were a $36 million net benefit (from the 25 percent reduction in O_3) and a $157 million loss (from the increase in O_3). The 0.05 ppm analysis amounted to a slight degradation in air quality and hence a very small economic loss. These effects are in line with those observed in Adams et al. (1982), but are based on more defensible biological data on plant response.

The second study, by Rowe et al. (1984), focused on both annual and perennial crops in the San Joaquin Valley of California, the major production area of the state. Using both field (county average yields, climatic, and economic data) and experimental data from NCLAN and other researchers, Rowe et al. (1984) estimated a series of yield functions for the major crops grown in the San Joaquin Valley for both O_3 and sulfur dioxide (SO_2). With the exception of potatoes, no yield changes were seen from adjustments in ambient SO_2 levels. Ozone exposure was characterized as a cumulative seasonal dose recorded during a daily 8-hr period. The yield adjustments associated with three O_3 reduction scenarios were then used to drive the same economic programming model used in Howitt et al. (1984a,b).

The O_3 analyses of Rowe et al. (1984) feature greater reductions and hence greater yield adjustments than those in Howitt et al. (1984a,b), as well as broader crop coverage. As a result, the benefits of control are larger (though still a small proportion of agricultural value), amounting to $48 to $117 million, depending on the ambient O_3 level assumed. These results, in combination with earlier California studies, provide evidence of economic consequences of O_3, with the distribution of these impacts felt most heavily by the producers of the commodities. For example, in both Howitt et al. (1984a,b) and Rowe et al. (1984), producer impacts are about 60 to 70 percent of the total change in economic surplus. The Rowe et al. (1984) study also provides some support for the use of combined field and experimental data as a means of filling gaps in the generation of yield effects for a broad range of crops.

The economic consequences of air pollution to agriculture within the Ohio River Basin (Illinois, Indiana, Ohio, Kentucky, West Virginia, and Pennsylvania) were estimated by Page et al. (1982). The region is a major producer of corn, soybeans, and wheat; it also experiences O_3 levels sufficiently high to depress crop yields. Page et al. (1982) examined a wide range of energy use scenarios that may occur in the Ohio River basin. These were then translated into changes in ambient air quality. Regional supply curves were estimated for each crop, based on standard economic specification of such relationships. These supply curves were then shifted to reflect varying air pollution assumptions. The change in area above these curves and below a given price represent the producer surplus change for such a shift in supply. While the study included two pollutants, SO_2 and O_3, approximately 98 percent of the losses were attributed to O_3.

The magnitude of the supply shifts, and hence producer economic effects, was based on yield response data provided by Loucks and Armentano (1982). The response functions from Loucks and Armentano (1982) used to generate the supply adjustments were synthesized from experimental data from other researchers for these crops and then applied to air quality data for the Ohio River Basin. Economic losses were measured as changes in producers' surplus resulting from supply curve shifts between clean-air and O_3 and SO_2 levels under the varying scenarios. The net present value of O_3-induced losses between clean air (a background of 0.03 ppm) and the various air quality scenarios for the period (1976 to 2000) is approximately $7.0 billion, or an annual equivalent of $278 million. Not surprisingly, most of these losses accrue to the states with the largest agricultural production in the region, Illinois and Indiana.

Several limitations need to be noted concerning the response data and the economic estimates of Loucks and Armentano (1982). First, the use of these supply adjustments in the Ohio River Basin represents an extrapolation of data from other regions and cultivars that may not be typical of the Ohio River Basin. Further, an ex post comparison with NCLAN data indicates that the predicted yield changes used here do not conform well to the subsequent NCLAN data; i.e., the yield adjustment estimates of Loucks and Armentano (1982) are higher than those for current NCLAN response functions. Second, in addition to problems with the underlying response data, there is a conceptual problem associated with assessing only producer level effects. While Page et al. (1982) noted that this region produces over a third of U.S. corn and soybeans, they assumed that there would be no price effects associated with changes in supply. This assumption is questionable in view of the other recent studies in the region that have demonstrated a price effect for supply shifts of this general magnitude. These other results suggest that the study probably overstated producer effects while ignoring potentially large changes in consumer welfare.

Benson et al. (1982) have provided estimates of the economic effects of O_3 on Minnesota agriculture. The plant science assumptions for the study were summarized in Section 6.4.3.2.2. The authors evaluated O_3-induced crop losses for alfalfa, wheat, corn, and potatoes through the application of crop loss functions that specifically accounted for crop development and episodic exposure by breaking exposure into multiple time periods over the growing season. The approach was similar to that used by Loucks and Armentano (1982) in that raw data on yields and O_3 exposure from other researchers (at sites outside Minnesota) were used to develop crop loss models under different measures of exposure and different functional forms. The loss functions were then applied to Minnesota by using actual or simulated 1979-1980 county-level O_3 data for Minnesota. The results of this procedure are subject to the same limitations noted for the Page et al. (1982) study.

The potential production losses for each county were aggregated by Benson et al. (1982) to provide a statewide crop loss measured in physical units. An economic model of supply and demand relationships for U.S. agriculture was then used to convert these production adjustments for each crop into producer losses, under two alternative supply assumptions: (1) assuming O_3 levels and thus production are unchanged in areas outside of Minnesota; and (2) assuming that O_3 levels and therefore yields change nationwide. In the second case, the analysis accounted for supply and demand relationships for each crop as affected by production changes in all regions. The two assumptions gave highly divergent estimates of economic effects on Minnesota producers. For example, the estimated dollar loss to Minnesota producers attributable to a worst-case O_3 level obtained from the first assumption was approximately $30.5 million in 1980 dollars. When, however, the economic model accounted for price increases resulting from reduced production in Minnesota and all other regions, there was a gain to Minnesota producers of $67 million in the short run if O_3 levels increased (in Minnesota as well as other production areas). This gain resulted from the rise in prices associated with reduced supply. These results, when combined with similar observations from Adams et al. (1982) and Leung et al. (1982), suggest the importance of using assessment methodologies that account for regional market linkages and resultant price effects.

Mjelde et al. (1984) estimated the effects of O_3 on Illinois cash grain farms (farms producing corn, soybeans, and wheat but no livestock) by estimating income and cost relationships for individual farms exposed to various levels of O_3. One objective was to test whether a meaningful link could be established between the physical loss estimates obtained under controlled experimentation, such as in the NCLAN program, and response information inherent in observed economic behavior (i.e., the individual farmer's cost and yield data). To test for such a link, the authors developed profit and cost functions (functional relationships in which profit or cost is regressed on economic and environmental explanatory variables) based on data from a large sample of Illinois grain farms. These profit and cost relations were estimated from actual cost and production data for these Illinois farms and incorporated environmental variables (i.e., O_3, temperature, and rainfall) as well as traditional economic variables. Data on O_3 for each year were prepared by J. Reagan, U.S. Environmental Protection Agency, via the Kriging spatial interpolation procedure (see Heck et al., 1982b). (Versions of this Kriged data set are used in several of the regional and national-level assessments.)

In most specifications of the profit functions, Mjelde et al. (1984) found a negative and significant (at the 5 percent level) impact by O_3 on profit. When the direct production (yield) effects of O_3 suggested by the farm-level sample data are compared with NCLAN results obtained in Illinois (the NCLAN site at Argonne National Laboratory), the production responses appear to be comparable. For a 25 percent increase in O_3, it was estimated by Mjelde et al. (1984) that physical output (a weighted average) of corn, soybeans, and wheat would decline 3.3 percent. The same 25 percent increase in O_3 used with NCLAN response functions predicts 11.7 percent and 3.7 percent decreases in output for two cultivars of soybean, while output of corn would decline between 1.4 and 0.6 percent for two cultivars. The Mjelde et al. (1984) estimate of 3.3 percent as a weighted average (weighted by the shares of corn, soybean, and wheat production for these Illinois farms) is quite similar to the NCLAN estimates.

In economic terms, the O_3 effects found in the Mjelde et al. (1984) analysis resulted in an annual aggregate loss in profits to Illinois farmers of \$55 to \$220 million, depending on O_3 levels in a given year (from 1976 to 1980). While the results suggest that economic estimates can be obtained without complete reliance on experimental data for all crops and cultivars in a region, certain caveats need to be noted. First, by current standards, the authors had abundant economic and air quality data with which to work. Such detailed data on producers' costs and yields do not exist at the national level. In addition, a number of statistical and estimation problems arose. Even though some of these were resolved, the stability of the coefficients in several specifications is suspect and reinforces some well-recognized difficulties in using secondary data to sort out statistically the effect of one environmental variable from among the many that affect yield. Also, even without statistical difficulties, the methodology does not eliminate the need for experimental data, as some form of detailed experimental data is needed to establish the plausibility of the regression estimates. Finally, from an economic standpoint, the study suffers a conceptual problem similar to that in Page et al. (1982), that is, no price changes (from changes in O_3) are calculated; hence, probable effects on consumers are ignored.

In a study of the effects of O_3 on Corn Belt agriculture, Adams and McCarl (1985) used a mathematical programming model of U.S. agriculture to measure effects of alternative O_3 standards on producers and consumers. The model is conceptually similar to the programming models in Adams et al., (1982), Howitt et al. (1984a,b), and Rowe et al. (1984). The model is more detailed, however, in its representation of both producer and consumer level responses. Further, the model is applicable to the entire U.S. agricultural sector, including livestock and export markets. In Adams and McCarl (1985), changes in yields for corn, soybeans, and wheat in the Corn Belt were predicted with NCLAN O_3 concentration-response data through 1982. Ambient 1980 O_3 levels, measured as a seasonal 7-hr average, were obtained from the same Kriged data set used in the Mjelde et al. (1984) study. Assuming no yield changes in the rest of the U.S., the results of the analysis suggested that a reduction in ambient O_3 from the present Federal standard of 0.12 ppm to 0.08 ppm would provide a net benefit (increase) in economic surplus of \$668 million. Conversely, relaxing the standard to 0.16 ppm would result in a reduction in economic surplus of approximately \$2.0 billion. The bulk of the benefits came from changes in soybeans yield; soybeans are much more yield-sensitive to O_3 than corn. The results of this analysis are consistent with distributional shifts associated with changes in supply in the face of inelastic demand. That is, the 0.08 ppm scenario benefits consumers at the expense of producers, whereas the 0.16 ppm assumption results in the opposite. These changes in Federal standards are portrayed by assumed seasonal 7-hr O_3 levels (across the entire Corn Belt) of 0.04 ppm and 0.075 ppm. This translation of a 1-hr standard into a seasonal 7-hr average is tenuous and assumes a lognormal distribution of O_3 events. In reality, then, these estimates are for reductions in O_3, rather than actual changes in Federal standards.

The authors also performed sensitivity analyses (i.e., compared changes in the model output to changes in model parameters) to test the effect of different yield data and assumptions on the economic estimates generated by the model. The results of such analyses indicated that the effect of the plant science data (or yield predictions) on economic estimates varied dramatically. Specifically, the authors compared economic surplus estimates generated from response data on corn and soybeans in the literature prior to NCLAN with estimates using actual NCLAN data, and observed a large difference. Conversely, when estimates using different subsets of NCLAN data were compared, the effect of additional data on a given crop was less important, and in some cases was trivial. One implication of this analysis is that the error in some early economic estimates based on biological responses extrapolated from other crops or not cross-checked against experimental data may be quite large.

6.5.4.2 Review of National Assessments. National analyses can overcome a fundamental limitation of regional analyses by accounting for economic linkages between groups and regions. Accounting for these linkages, however, requires additional data and more complex models, and frequently poses more difficult analytical problems. Thus, detailed national assessments tend to be more costly to perform. As a result, there are fewer assessments in the literature of pollution effects at the national than at the regional level.

Of the national assessments performed since the last criteria document was published (U.S. Environmental Protection Agency, 1978), two use the traditional "price times quantity" approach to quantify dollar effects. Analyses of this type are deficient in capturing the true economic concept of benefits, as discussed earlier. Four of the most recent national assessments included in this review, however, use more defensible measures of economic effects. Both types of national-level estimates of O_3 damages are summarized in Table 6-32. As with Table 6-31, considerable information on the nature of

TABLE 6-32. SUMMARY OF ESTIMATES OF NATIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study	Crops and no. of cultivars	Annual benefits of control ($billion)	Plant response data	Aerometric data	Economic model/data	Additional comments
Ryan et al. (1981)	16 crops: alfalfa, beets, broccoli, cabbage, corn (sweet and field), hay, lima beans, oats, potatoes, sorghum, soybeans, spinach, tobacco, tomatoes, wheat. Specific response data available for only 5 crops, and one cultivar for each of these crops (see "Plant response data" column).	$1.747 (in 1980 dollars).	Yield-response information derived from a synthesis of 5 yield studies in the literature prior to 1980. Synthesized response functions estimated for both chronic and acute exposures. The 3 chronic response functions and 2 acute response functions are extrapolated to cover 6 of the 16 crops. For the remaining 10 crops, surrogates from the respective chronic and acute functions are used. Yield changes are based on reduction in O_3 to meet 1980 Federal standard of 0.12 ppm in noncompliance counties.	Dose measured in several ways to correspond to underlying response function. Acute doses measured as concentrations within a given averaging time or second highest 8-hr average. O_3 data derived from several sources, including data from National Aerometric Data Bank and from Lawrence Berkeley Laboratory, for period 1974-1976. Exposures calculated for only those counties (531) exceeding the Federal standard (0.12 ppm).	Naive economic model. Monetary impact calculated by muitiplying changes in county production by crop price in 1980. Measures impact on producers only.	Dollar estimate is for the 531 counties exceeding the Federal standard of 0.12 ppm. This study is essentially an updated version of Benedict et al. (1971) reported in the 1978 criteria document (U.S. Environmental Protection Agency, 1978).
Shriner et al. (1982)	4 crops: corn, soybeans, wheat, and peanuts. Multiple cultivars of all crops but peanuts.	$3.0 (in 1978 dollars).	Analysis uses NCLAN response data for 1980. Functions estimated in linear form. Yield changes reflect difference between 1978 ambient O_3 levels of each county and assumed background of 0.025 ppm concentration.	Dose measured as 7-hr average to be compatible with NCLAN exposure levels. Rural ambient concentrations for 1978 estimated by Kriging procedure applied to SAROAD data.[a]	Same as Ryan et al. (1981), except uses 1978 crop prices.	Dollar estimates are for all counties producing the four crops. As with Ryan et al. (1981), estimates are for producer-level effects only.
Adams and Crocker (1984)	3 crops: corn, soybeans, and cotton. Two corn cultivars, three soybean, two cotton.	$2.2 (in 1980 dollars).	Analysis uses NCLAN O_3-yield data for 1980 and 1981. Functions estimated in linear form. Yield changes measured between 1980 ambient levels and an assumed O_3 concentration of 0.04 ppm across all production regions.	Dose is measured as the seasonal 7-hr average to be compatible with NCLAN experiments. 1980 ambient O_3 levels estimated by Kriging of SAROAD monitoring sites, translated into a seasonal 7-hr average.	Economic model consists of crop demand and supply curves. Yield changes are used to shift supply curve. Corresponding price and quantity adjustments result in changes in economic surplus. No producer-level responses modeled; only measures aggregate effects.	Economic estimate measured in terms of changes in consumer and producer surpluses associated with change in O_3.

TABLE 6-32 (cont'd). SUMMARY OF ESTIMATES OF NATIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study	Crops and no. of cultivars	Annual benefits of control ($billion)	Plant response data	Aerometric data	Economic model/data	Additional comments
Adams et al. (1984a)	4 crops: corn, soybeans, wheat, and cotton. Two cultivars for corn and cotton, three for soybeans and wheat.	$2.4 (in 1980 dollars).	Analysis uses NCLAN O_3-yield data for 1980 through 1982. Yield changes measured between 1980 ambient levels and 25% reduction in O_3 across all regions. Functions estimated in both linear and quadratic form.	Same as Adams and Crocker (1984).	Same as Adams and Crocker (1984), except that analysis examines range of economic estimates reflecting variability in yield predictions resulting from sample size and functional form.	Same as Adams and Crocker (1984). Linear functions result in higher yield losses and hence higher economic loss estimates. Reported estimate ($2.4 billion) is for quadratic response function.
Kopp et al. (1984)	5 crops: corn, soybeans, wheat, cotton, and peanuts. Multiple cultivars of each crop except peanuts.	$1.2 (in 1978 dollars).	Analysis uses NCLAN O_3-yield response data for 1980 through 1982. Response data are estimated in a Box-Tidwell flexible functional form. Yield losses (for estimates reported here) measured as the difference between ambient 1978 O_3 and a level assumed to represent compliance with a 0.08 ppm standard.	Same as Adams and Crocker (1984) and Adams et al. (1984a), but for 1978 growing season.	Economic model consists of detailed producer-level models, by crop, for numerous production regions. Predicted yield changes are used to generate supply shifts for each region/crop. Aggregate supply shifts are then combined with crop demand relationships to estimate changes in producer and consumer surpluses.	In addition to measuring the change in economic surplus for various assumed O_3 levels, the analysis also includes an examination of the sensitivity of the estimates to the nature of the demand relationships used in the model.
Adams et al. (1984b)	6 crops: barley, corn, soybeans, cotton, wheat, and sorghum. Multiple cultivars used for each crop except barley and grain sorghum; two for cotton, three for wheat, two for corn, and nine for soybean.	$1.7 (in 1980 dollars).	Analysis uses NCLAN O_3-yield response data for 1980 though 1983. Response functions are estimated in Weibull form. For soybeans, both individual and pooled cultivar responses are estimated. Yield changes reflect changes from 1980 ambient O_3 of 10, 25, and 40% reduction and a 25% increase for each response.	Same as above but for 1980, and 1976 through 1980 periods.	Economic model consists of two components: a series of farm-level models for each of 55 production regions and a national model of crop use and demand. Yield changes are used to generate regional supply shifts for farm-level models. These supply responses are then used in the national model.	Consumer surplus estimated for both domestic and foreign markets; producer surplus nationally and by region. The analysis includes a range of economic estimates reflecting changes in response and O_3 data and assumptions. This sensitivity analysis identifies stability of analysis results with respect to various parameters.

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[a] Kriging is a spatial interpolation procedure that has been used to generate O_3 concentration data for rural areas in which no monitoring sites have been established. See Heck et al. (1983b).

critical plant science, aerometric, and economic data is presented, along with the actual estimates of benefits or damages. It is apparent from the table that the range of estimates is relatively small. Such relative consistency does not necessarily imply convergence on the "true" economic effects, however, as the analyses employ somewhat different crops, response information, and assessment approaches, as detailed below.

The recent national-level economic estimates of the effects of O_3 on agriculture include an assessment for the National Commission on Air Quality (Ryan et al., 1981). This is an updated version of the Benedict et al. (1971) study cited in the 1978 criteria document (U.S. Environmental Protection Agency, 1978). The purpose was to estimate the benefits of meeting the SNAAQS for O_3 and SO_2 accruing to 16 agricultural crops. The principal methodological differences between this study and the earlier Benedict et al. (1971) approach include the use of a wider range of dose-response functions drawn from the plant science literature through 1980, updated production data from the 1974 Census of Agriculture, and updated air quality and price information.

The loss in potential yield and hence total production as a result of O_3 and SO_2 pollution was estimated using alternative response functions and county-level data on air quality for counties that have not attained SNAAQS (531 counties). The response functions were of two types: chronic and acute. Each was taken from existing data, with the acute based on foliar-injury response models linearly converted to yield response. Only five crop-specific studies were cited as sources for the response functions used in the analysis, with the response of the remaining 11 crops (of the 16 studied) predicted by surrogates selected from the five for which data were available. The predicted physical loss estimates were then translated to a dollar value by the ad hoc procedure of multiplying the reduction in production by the 1980 crop price for each commodity. The resultant dollar loss estimate (or potential benefit of meeting the SNAAQS for O_3 and SO_2) was estimated to be \$1.8 billion in 1980 dollars for agricultural crops. Of this total, the benefits of meeting the O_3 standard are far greater than the direct benefits of meeting SO_2 standards (\$1,747 million compared to \$34 million), because the number of nonattainment counties for O_3 is nearly six times the number of nonattainment counties for SO_2, and because fewer crops show sensitivity to SO_2. This estimate is much higher than the Benedict et al. (1971) estimate, reflecting the sensitivity of these estimates to the data assumptions and time period employed. Note that this entire amount is assumed to accrue to producers, as the calculation procedure does not measure consumer effects.

Besides the use of a deficient methodology, another shortcoming of this assessment (Ryan et al., 1981) is that the crop yield-response estimates are generated from a very limited set of actual data, reflecting the sparseness of data prior to the availability of NCLAN data. The use of foliar-injury models and the extrapolation across a large number of crops are obvious sources of uncertainty. In view of the improved data and assessment frameworks currently available, this monetary estimate is much less defensible than more recent estimates.

A national assessment by Shriner et al. (1982) for the Office of Technology Assessment of the U.S. Congress estimated the losses associated with ambient O_3 levels for four crops: corn, soybeans, wheat, and peanuts. The study employs NCLAN dose-response functions (in linear form) for each crop. Although the data used were taken from only the first year of the NCLAN program, those first-year data were generated under consistent conditions across all crops, making the yield responses more plausible than the mixed, often extrapolated sets (using one crop to portray response of other crops) used by earlier researchers. The study also used county-level O_3 data interpolated by Kriging from data obtained at SAROAD rural monitoring sites. Agricultural yields and production by county were adjusted from 1978 actual yields (as reported in the 1978 Census of Agriculture) using the NCLAN response functions and the county-level O_3 data. Changes in yield were measured against what the yields would be if crops were exposed to a "background" ambient O_3 level of 0.025 ppm. As in the Ryan et al. (1981) study, the estimated reductions in county production levels for each crop were then converted to a monetary estimate of loss by the traditional procedure of multiplying by constant county-level price. The aggregate monetary loss (or difference between values of production at ambient levels of O_3 and those at 0.025 ppm) for the United States was estimated at approximately $3 billion. This estimate suffers from the same problems as those associated with the Ryan et al. (1981) study and other studies that abstract from economic factors. Also, the calculation of the seasonal 7-hr averages from the SAROAD sites (for use with the NCLAN response functions) appears to have been inflated by use of a daily 7-hr maximum, rather than the 7-hr average. This would result in a larger difference between ambient and background O_3 and an inflation of the yield adjustments. The principal improvement of the Ryan et al. (1981) study over the Benedict et al. (1971) assessment, thus, is the use of 1980 NCLAN data and an aerometric data set that is based on actual rural ambient O_3 levels, even though the data may possibly be slightly biased.

Another estimate of O_3 effects on agriculture was developed by Adams and Crocker (1984), who used information on O_3-induced plant effects to determine the sensitivity of resultant economic estimates to additional plant response information. The study also presents a numerical estimate of O_3 damage to corn, soybeans, and wheat, representing about 60 percent of the value of U.S. crop production. Response data for these crops were derived from 1980 and 1981 NCLAN experiments. Response functions were estimated in linear form.

Rural O_3 ambient levels for 1980 were derived from a corrected version of the Kriged data set used in the Shriner et al. (1982) study. The predicted yield changes for reduction in O_3 to an assumed ambient concentration of 0.04 ppm were introduced into a simple economic model of farm-level demand and supply functions. The predicted yield changes were used to shift supply, which, when combined with the demand relationships for the commodity markets in question, generated estimates of the economic surplus accruing to consumers and producers from reductions in O_3. The estimated difference between ambient O_3 levels associated with the current standard of 0.12 ppm (as measured from the Kriged SAROAD monitoring data) and a seasonal 7-hr average of 0.04 ppm was approximately $2.2 billion in 1980 dollars. This calculation assumes that all rural areas achieve the 7-hr seasonal average of 0.04 ppm O_3, which is unlikely. Also, the economic model measures price effects but lacks any detail on individual producer or consumer responses. Both aerometric assumptions and this economic abstraction imply an upward bias to the estimates.

Another national-level estimate of the economic consequences of O_3 on corn, soybeans, cotton, and wheat is reported in Adams et al. (1984a). This study used essentially the same methodology used by Adams and Crocker (1984). While the primary purpose of the analysis was to discuss and measure the role of plant science information in economic assessments, the analyses included the estimated measurement of the benefits of changing O_3 exposures for the four crops. Ambient O_3 levels for 1980 were characterized as the seasonal 7-hr average and were taken from the Kriged data set. The benefits were measured in terms of economic surplus estimated from the integration of supply and demand curves for each crop under the alternative O_3 levels. Yield effects from both linear and quadratic response functions were used to shift the respective crop supply curves under alternative O_3 scenarios. The new intersections of supply and demand then generated changes in economic surplus.

The benefit of an assumed reduction in ambient O_3 from 1980 estimated levels to 0.04 ppm across the entire U.S. was estimated by Adams et al. (1984a) to be approximately \$2.4 billion in 1980 dollars. A 25 percent increase in O_3 (to 0.066 ppm) resulted in a net loss of \$3.0 billion. These estimates were derived with quadratic functional forms of the response model; linear estimates were approximately 40 to 50 percent higher. Like the Adams and Crocker (1984) study, these estimates are probably upper bounds, in that the economic model does not deal with the specific types of producer responses that may mitigate for changes in O_3. Nor does the model fully take into account certain factors that potentially distort the agricultural markets, such as the Federal farm program (which typically changes from year to year). It does include, however, direct transfer payments to farmers from the U.S. Treasury that are part of the Federal farm program. The analysis uses averaged assumed current ambient concentrations for all production regions, rather than individual county or subregion levels. The averaged ambient levels are the upper-bound seasonal 7-hr concentrations for major production areas as reported in the SAROAD data. To the extent that all regions are equal to or less than this amount, the benefits of reductions in O_3 are overstated and the losses from O_3 increases are understated.

The studies reviewed to this point all suffer in various degrees from either plant science and aerometric data problems, incomplete economic models, or both. Some were not intended to provide estimates for use in policy evaluation. As a result of these limitations, decision-makers should be cautious in using these estimates to evaluate the efficiency of alternative SNAAQS. There are, however, two recent EPA-funded studies that overcome most of the problems plaguing the above assessments. Together, they provide better estimates of the agricultural consequences of changes in ambient O_3. Each is reviewed below.

The first of these is a recent assessment by Kopp et al. (1984) that measured the national economic effects of changes in ambient O_3 levels on the production of corn, soybeans, cotton, wheat, and peanuts. The study is notable for several reasons. First, the assessment methodology was based on the development of a series of detailed farm-level representations of costs and yield for approximately 200 production regions for these crops, using the Farm Enterprise Data System (FEDS) surveys from the U.S. Department of Agriculture

(USDA). These farm-level responses were then aggregated to regional and national supply responses. The use of farm-level models to initiate the analysis is important in that it places emphasis on developing reasonable micro- or producer-level responses to externally induced yield changes, such as those that may be associated with changes in O_3. Second, the effects of O_3 on the yields of the included crops were based on NCLAN data through 1982. Instead of using the Weibull models of the NCLAN program, response functions of the Box-Tidwell type were fitted to these data. Predicted yield changes associated with alternative secondary standards were then used to shift the regional supply-response relationships. The price and consumption effects were measured through a set of demand relationships for each commodity, reflecting a range of elasticity assumptions, as reported by the USDA.

The results of the analysis indicate that a reduction in O_3 from regional ambient levels (as portrayed by the Kriged SAROAD set) (Heck et al., 1983b) to an approximate 0.04 ppm seasonal 7-hr average would result in a $1.2 billion net benefit in 1978 dollars. Conversely, an increase in O_3 to an assumed ambient concentration of 0.08 ppm across all regions would produce a net loss of approximately $3.0 billion. The benefit estimate of O_3 reductions is slightly less than the estimates reported in Adams and Crocker (1984) and Adams et al. (1984a). The differences may be attributable to the more detailed regional and farm-scale resolution in Kopp et al. (1984), as well as different base years (1978 versus 1980), different ambient base O_3 levels, and different elasticity assumptions vis-à-vis these other studies. Relative to previous assessments, limitations of this analysis are minor but include the lack of crop substitution possibilities between sensitive and tolerant crops, and the forcing of the economic adjustment process onto what is perceived to be the high-cost production region. In addition, the study does not consider the impact of Federal farm programs on benefits estimates. The analysis provides, however, a detailed representation of the economic processes underlying agricultural production, uses the most complete biological and aerometric data currently available, and is directed toward providing useful policy analyses of O_3 pollution.

The second study, by Adams et al. (1984b, 1985), is a component of the NCLAN program. As such, the analyses, data, and results contained in this assessment represent the collective biological, meteorological, and economic data assembled in the NCLAN program through 1983. The results were derived from an economic model of the U.S. agricultural sector (adapted from Chattin et al., 1983) that included domestic consumption, export use, and livestock feeding and processing. Farm-level behavior was portrayed by individual farm models for 55 production regions. The analysis looked at six major crops (corn, soybeans, wheat, cotton, grain sorghum, and barley) that account for over 75 percent of U.S. cropped acreage. Potential O_3 effects on hay were also evaluated using the average yield response of other crops as a surrogate. The model output included estimates of the changes in crop production, prices, and economic surpluses, by crop and region.

Ozone-induced yield changes for each crop and region, as defined by NCLAN response functions (in Weibull form), were used in the economic model to estimate economic effects resulting from those O_3 changes. Four hypothetical O_3 scenarios (three reductions, one increase) were judged against a 1980 ambient O_3 base solution. The difference between the base solution, reflecting 1980 parameters, and the hypothetical O_3 analyses provided an estimate of the benefits or costs of the changes in O_3 levels. The results indicated that the annual benefits (in 1980 dollars) to society from O_3 adjustments are substantial, but represent a relatively small percentage of total agricultural output (about 4 percent). Specifically, a 25 percent reduction in O_3 from 1980 ambient levels resulted in benefits of $1.7 billion. This estimate is quite close to the Kopp et al. (1984) benefit estimate (when Kopp et al. dollars are converted to 1980 dollars), suggesting that benefits of O_3 reductions are of this magnitude. A 25 percent increase in O_3 resulted in an annual loss (negative benefit) of $2.363 billion.

In addition to estimating a set of economic effects for the four O_3 scenarios, the assessment by Adams et al. (1984b, 1985) also included some measure of the sensitivity of the economic estimates to assumptions concerning response and O_3 data. The sensitivity analyses addressed the use of alternative cultivar response functions (rather than average "pooled" responses), use of different ambient O_3 levels, and the potential influence of moisture stress on O_3 yield estimates. The effect on economic estimates, compared with the above estimates, ranged from trivial to substantial (from less than 5 percent difference to approximately a 50 percent difference). The greatest sensitivity was reflected in an analysis in which yield predictions were taken from the most extreme cultivar response available for soybeans, corn, wheat, and cotton. Here the benefits of a 25 percent O_3 reduction rose to $2.7 billion. Statistically and agronomically, however, these cultivar (yield) responses behave unlike responses of the other NCLAN cultivars for those crops. As such, these higher economic estimates are perhaps upper bounds on potential impacts.

While the estimates from both Kopp et al. (1984) and Adams et al. (1984b, 1985) are derived from conceptually sound economic models, there are several sources of uncertainty or error. These include the issue of exposure dynamics (7-hr seasonal mean from the NCLAN experiments versus other exposure statistics and exposure periods) and the lack of environmental interactions, particularly O_3-moisture stress interactions, in many of the response experiments. Also, the O_3 data in both studies are based on a limited set of SAROAD monitoring sites, mainly in urban and suburban areas. While the spatial interpolation process (Kriging) results in a fairly close correspondence between predicted and actual ozone levels at a few validation points, there is a need for data from more monitoring sites in rural areas. The economic models, with their large number of variables and parameters, and the underlying data used to derive these values, are potential sources of error; e.g., sensitivity analyses on demand elasticities by Kopp et al. (1984) and on foreign exchange rates (export market conditions) by Adams et al. (1984b) indicate changes of up to about 20 percent. In addition, neither study, Kopp et al. (1984) nor Adams et al. (1984b), considers the impact on benefits estimates of the Federal farm subsidy program and other factors that may upset free-market equilibria and produce market distortion. The Adams et al. (1984b) model is a long-run equilibrium model and assumes that supply will be consumed at some price. Its policy utility is greatest when addressing changes bounded by historical levels, rather than quantum adjustments. The adjustments portrayed, however, in the O_3 analyses by Adams et al. (1984b) fall within these historical levels.

6.5.5 Overview of Current Economic Assessments of Effects of Ozone on Agriculture

The ability to assess O_3 damage to agricultural crops has been greatly enhanced by recent improvements in crop yield-response information and air quality data. As Section 6.4.3.2.2 of this chapter indicates, the plant science literature now contains concentration-response functions calibrated in yields for most major agricultural commodities, primarily as a result of the NCLAN program. While cultivar coverage remains sparse for some crops and important edaphic-climatic interactions are only partially addressed, these concentration-response relationships are superior to data underlying loss estimates reported in the 1978 criteria document. In addition, air quality data for rural areas have improved as monitoring expands. Interpolation procedures, such as the use of Kriging based on SAROAD information, offer promise in terms of filling existing gaps in air quality data.

This review of recent agricultural assessment efforts also indicates an increase in the application of techniques consistent with economic theory. Consequently, the studies produce more defensible estimates of economic benefits. Two of the most recent studies, those by Kopp et al. (1984) and Adams et al. (1984b), are the most comprehensive economic assessments of O_3 damages performed to date. In even these studies, however, as well as in other studies reviewed in this section, the treatment of some economic and plant science issues is not complete. Some deficiencies include the need to measure damages to perennial crops (fruits and nuts, forests); and the need to account for potential long-term and dynamic O_3 effects, such as interactions between O_3 levels and the frequency and intensity of insect and disease incidence, rainfall or irrigation patterns, and fertilizer and other factors. Such effects might differentially alter producer patterns in the use of irrigation and the application of pesticides and fertilizer, a possibility not currently addressed in economic assessments (all assume O_3 neutrality with respect to input use). Also requiring more attention are potential economic damages to nonmarketed plants (e.g., as manifested through aesthetic effects on forest ecosystems). As noted earlier, another important issue concerns the appropriate measure of dose. While the current NCLAN experimental design (as discussed in this chapter) uses the seasonal 7-hr mean concentration, other dose measures may better characterize plant response and lead to different predicted yield changes. Furthermore, the NCLAN response functions for individual crop cultivars estimated at various sites appear to be relatively homogeneous when measured in percentage change (rather than absolute values), but the validity of extrapolating site-specific response data across regions is not fully resolved. Finally, the impact of factors that result in market distortions, such as the Federal farm subsidy programs, have not been addressed.

Nevertheless the inclusion of these possible improvements in future assessments is not likely, with the possible exception of market-distorting factors, to alter greatly the range of agricultural benefits provided in the Kopp et al. (1984) and Adams et al. (1984b) studies, for several reasons. First, the current studies cover about 75 to 80 percent of U.S. agricultural crops (by value). For inclusion of the other 20 percent to change estimates greatly would require that their O_3-sensitivity be much greater than that for the crops included to date. Second, the model sensitivity analyses from existing studies indicate that changes in key plant science parameters must be substantial to translate into major changes in economic estimates. From experience to date, it seems unlikely that use of different dose measures or interaction effects would result in changes of the magnitude already addressed in some of the sensitivity analyses. Third, even if there are such changes, there are likely to be countervailing responses; e.g., longer exposure periods may predict greater yield losses but O_3-water stress tends to dampen or reduce the yield estimates. Finally, it should be noted that potential improvements in economic estimates of agricultural effects are relevant to policy only to the extent that they alter the relationship between total benefits and total costs of that policy. Uncertainties in other effects categories (non-agricultural) are probably greater.

In conclusion, the recent economic estimates of benefits of O_3 control to agriculture, particularly those by Kopp et al. (1984) and Adams et al. (1984b), provide the most defensible evidence appearing in the literature to date of the general magnitude of such effects. The close correspondence of the Kopp et al. (1984) and Adams et al. (1984b) estimates also indicates that sound economic models are available for application to this problem area. As a percentage of the total value of crops included in these assessments, the loss estimates are in the range of 4 to 6 percent. This is comparable with the estimates of crop losses from sources such as insects and diseases reported by Boyer (1982) but far less than the $25 billion annual loss attributed by the U.S. Department of Agriculture (1965) to weather-related damage. Relative to estimates in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) and economic information on other O_3 effects categories, such as damage to materials, these two studies, in combination with the NCLAN data on yield effects, provide the most comprehensive economic information to date on which to base judgments regarding the economic efficiency of alternative SNAAQS. As noted in this review, there are still gaps in plant science and aerometric data and a strong need for meteorological modeling of O_3 formation and transport processes for use in formulating rural O_3 scenarios. With regard to the economic data and models used, the impact of factors that upset free-market equilibria needs further analysis. Additionally, it must be emphasized that none of the studies has accounted for the compliance costs of effecting changes in O_3 concentrations in ambient air. A complete benefit-cost analysis requires that the annualized estimated benefit to agriculture that would result from ozone control be combined with benefits accruing to other sectors and then compared with the overall annualized compliance costs.

6.6 MODE OF PEROXYACETYL NITRATE (PAN) ACTION ON PLANTS

Peroxyacetyl nitrate (PAN) is the most common member of a series of homologues that increase in phytotoxicity with increase in molecular weight. Only PAN is found in ambient air at concentrations of possible concern, and then only in limited areas of the country.

The sequence of events inducing vascular plant response to PAN is essentially identical to that described for O_3 (Section 6.3); PAN enters the leaf tissue through open stomata and dissolves in the aqueous layer surrounding the substomatal chamber (Figure 6-1). Hill (1971) reported that PAN was relatively insoluble and that the rate of absorption by an alfalfa canopy was approximately one-half that for O_3. The absorption rate depends upon the ability of the plant to metabolize, translocate, or otherwise remove the active pollutant species from the absorbing solution, as well as on the solubility of PAN. Thus, the flux of PAN into the inner leaf tissues is influenced by many physical, biochemical, and physiological factors. The equation used to describe O_3 flux (Section 6.3) also can be directly applied to describe the flux of PAN into the leaf.

Highly unstable, PAN breaks down rapidly when it comes in contact with an aqueous solution (Mudd, 1975). According to Nicksic et al. (1967) and Stephens (1967), the breakdown of PAN in aqueous solution yields acetate, nitrite, oxygen, and water. The pathway of PAN absorption and reaction within the leaf tissue has not been described well enough to explain why cells at a specific stage of physiological development are highly susceptible while adjacent cells are relatively tolerant. The magnitude of PAN injury is influenced by the stage of tissue development, succulence of the tissues, and conditions of the macro- and microclimate. Injury is manifested in several ways. The most evident injury is necrosis of rather specific areas of the lower and upper leaf surfaces. This characteristic symptom expression may be accompanied by leaf distortion, premature senescence, and defoliation (Taylor, 1969). Experimental evidence shows that yield may be suppressed in the absence of visible injury symptoms (Thompson and Kats, 1975; Temple, 1982). Symptoms of the type induced by PAN have been reported from California, the eastern United States, Canada, Japan, and the Netherlands (Table 6-33). The smog, photochemical smog, or oxidant injury symptoms described by Middleton et al. (1950), Went (1955), and by other researchers working with polluted ambient air in California prior to about 1960 were identical to injury symptoms subsequently produced with synthesized PAN (Taylor et al., 1961; Taylor, 1969). Frequently, the injury symptoms were sufficient to reduce significantly the quality of leafy vegetables and ornamental crops, but they were seldom associated with suppressed growth or yield.

The phytotoxicity of PAN and processes of injury development from PAN will be discussed in the following sections. Many of the biochemical and physiological studies with PAN and its homologues were conducted with concentrations that exceed those encountered in ambient air. The studies were conducted, however, to identify responses that might be more difficult to detect at lower concentrations. For unknown reasons, most vegetation grown in glass houses and growth chambers is considerably less sensitive to synthesized PAN than comparable plants grown and exposed to PAN and the total pollutant complex found in the field (Taylor, 1969).

6.6.1 Biochemical and Physiological Responses to PAN

As with O_3 (Section 6.3.1), the phytotoxic effects of PAN occur only when a sufficient amount of the gas diffuses into susceptible regions of the leaf interior and encounters the plasmalemma or passes into the liquid phase of the cells. Once deposited on the wet cell surface, the gas will begin to break down and the degradation products or PAN molecules, or both, will move by diffusion or bulk flow to sites of action (Mudd, 1975). The target sites may include the cell membrane, chloroplast, cytoplasm, and various cell organelles.

6.6.1.1 Gas-Phase Movement into the Leaf. The primary entry port for PAN into leaf tissue is through open stomata. As indicated in Section 6.3.1.1, the influence of O_3 on stomatal movement has received considerable attention, but relatively little effort has been made to determine if PAN will also induce stomatal closure. Starkey et al. (1981) reported that a PAN-susceptible variety of bean, exposed to 80 ppb PAN for 0.5 hr, developed drought stress symptoms but that a tolerant variety showed no effect. This finding suggests that PAN may have stimulated stomatal opening to allow a greater rate of transpiration. Metzler and Pell (1980) found that pinto bean plants exposed

TABLE 6-33. GEOGRAPHIC OCCURRENCE OF PAN/OXIDANT INJURY ON PLANTS[a]

Area	Species injured	Reference
California[b]	Bean, spinach, Romaine lettuce	Middleton and Haagen-Smit (1961)
Washington		
Missouri		
Illinois		
Colorado		
Utah[b]	Oat, petunia, tomato, Swiss chard, sugar beet	Tingey and Hill (1967)
Maryland	Tobacco	Went (1955)
Pennsylvania	Garden plants	
New York		
The Netherlands[b]	Little-leaf nettle, petunia, annual bluegrass	Floor and Posthumus (1977)
Japan[b]	Various species	Fukuda and Terakado (1974)
	Spinach, French bean, lettuce	Sawada et al. (1974)
Canada	Tomato	Pearson et al. (1974)

[a] Where a column entry is blank the information is the same as the entry above.

[b] Monitoring data for PAN in southern California, Utah, The Netherlands, and Japan were available to corroborate the reports of PAN-type symptoms observed in those areas.

to subthreshold levels of PAN (54 ppb for 1 hr) developed no macroscopic injury and showed no effects on stomatal conductance. At the injury threshold (70 ppb for 1 hr) and above, abaxial glazing developed and stomatal conductance increased. Temple (1982) observed no effects on stomatal conductance (compared to non-exposed plants) at concentrations of 25 and 50 ppb PAN after tomato leaves were exposed for 2 hr. In this study, 0.20 ppm O_3, in combination with the two concentrations of PAN, did suppress stomatal conductance when tomato plants were exposed for 2 hr.

The size of stomatal pores and number of stomata per unit area of leaf vary greatly according to plant species. Many plants have stomata in both surfaces of the leaf, whereas others have stomata only in the lower surface. As a general rule, stomata occur in larger numbers per leaf area near the apex of the leaf and become less numerous toward the base of the leaf. Although plants shown to be most susceptible to PAN are among those that have stomata in both leaf surfaces, no correlation between susceptibility and number or size of stomata has been demonstrated.

6.6.1.2 Biochemical and Physiological Responses. Peroxyacetyl nitrate is a highly specific phytotoxic agent that attacks leaf tissue at a fairly specific stage of physiological development and is most injurious to succulent, rapidly expanding tissues of herbaceous foliage (Noble, 1955; Taylor and MacLean, 1970). Concentrations of 14 to 15 ppb (maximum) under field conditions have been observed to produce PAN-type injury on susceptible crops (Taylor, 1969; Temple, 1982). Fukuda and Terakado (1974) reported that petunia plants under field conditions developed silvering and bronzing on the lower leaf surface when the maximum PAN concentrations ranged from 3.0 to 6.7 ppb. The most serious observed damage occurred when a PAN concentration of more than 5 ppb continued for 7 hr. Because PAN is phytotoxic at very low concentrations, Mudd (1963) concluded that the most likely target in plant cells must be some enzyme system. Much of the early work with enzymes involved the use of relatively high PAN concentrations to demonstrate reactive sites in the metabolic pathways.

Ordin (1962) observed that growth of oat coleoptile sections, which involved cell expansion rather than initiation of new cells, was inhibited by PAN. He found that fumigation with 1.1 ppm PAN for 6 hr resulted in 32 percent inhibition of growth and 45 percent inhibition of glucose absorption from the solution. Fumigations were accomplished by floating the oat coleoptiles in a solution and bubbling PAN through the solution. There was no way to determine how much PAN the coleoptiles actually encountered. The response suggests that PAN interfered with metabolism of cell wall sugars. Subsequently, Ordin and Hall (1967) found that cellulose synthetase was inhibited, and Ordin et al. (1967) reported that phosphoglucomutase was inhibited when coleoptile tissue was exposed to PAN. The treatment consisted of bubbling 50 ppm PAN for 4 hr at a rate of 400 ml/min through 100 ml of solution in which the coleoptiles were floating.

Using in vitro procedures, Mudd and Dugger (1963) showed that PAN oxidized NADH and NADPH. Mudd (1966) and Mudd et al. (1966) found that enzymes with free -SH groups were inactivated, but that enzymes with no free -SH groups were resistant to PAN. The amount of PAN used in these studies was not reported. Hanson and Stewart (1970) observed that exposure to 50 ppb PAN for 1 to 4 hr inhibited mobilization of starch in darkness, implying that the phosphorylase reaction was inhibited. Such a response could seriously interfere with photosynthate partitioning and thus could inhibit growth and development. The reaction deserves further investigation.

Thomson et al. (1965) showed that PAN (1000 ppb for 30 min) or its degradation products caused crystallization and other disruptions in the chloroplast stroma that were similar to the effects of dessication. These observations suggest that PAN affected the permeability of the chloroplast membrane in much the same way as it reacted with the plasmalemma, which allowed leakage of cell contents.

In summary, peroxyacetyl nitrate enters leaf tissue through open stomata, is rapidly dissolved in the aqueous covering of substomatal cells, and along with its degradation products is transported through the cell wall and cell membrane into the aqueous cell contents. The chloroplast membrane is disrupted, thereby inducing plasmolytic-type characteristics to develop. There is leakage of cellular fluids into the intercellular spaces. Enzymes containing sulfhydryl groups are inactivated by PAN. Visible injury from PAN results when mesophyll cells are killed and shrink, causing dessication and death of the epidermal tissue. A degree of chlorosis is often visible on the upper leaf surface as the chloroplasts in living cells are destroyed. The destruction of chloroplasts (Thomson et al., 1965) and disruption of biochemical and physiological systems (Ordin and Hall, 1967; Ordin et al., 1967; Mudd, 1966; Hanson and Stewart, 1970) can be expected to affect growth and yield adversely as well as the aesthetic qualities of the vegetation. Inactivation of enzymes can suppress growth, as demonstrated with oat coleoptiles, and may interfere with photosynthate, as demonstrated by inhibition of starch mobilization in the dark; and may interfere with other metabolic processes.

6.6.2 Factors that Modify Plant Response to PAN

Plant response to PAN and many other environmental stresses is conditioned by complex, interacting internal and external factors (U.S. Environmental Protection Agency, 1978). External physical factors such as temperature, light conditions, humidity, and edaphic factors can influence plant response to PAN. Similarly, biological variables such as genetic differences, physiological stage of tissue development, and rate of plant growth can affect plant response.

6.6.2.1 Biological Factors. Trees and other woody species are apparently quite resistant to foliar injury from PAN (Davis, 1975; Davis, 1977; Taylor, 1969). Foliar injury has been produced only once or twice by fumigations with extremely high concentrations of PAN (1 ppm for several hours), and injury to these species in the field has not been reported. Variations in susceptibility to PAN within herbaceous species have been observed in the field and have been demonstrated for some crops with synthesized PAN.

Genetically controlled plant variation to PAN has been observed under field conditions and verified by controlled PAN exposures. Drummond (1972) exposed 28 F_1 varieties of petunia plants to 150 ppb PAN for 1 hr and found highly significant differences in cultivar sensitivity. Six petunia cultivars that were common in the Boston area were exposed to high concentrations of PAN (120, 250, or 500 ppb for 1 hr) to ensure that all the cultivars developed some foliar injury so that differential cultivar sensitivity could be determined (Feder et al., 1969). The authors concluded that the cultivars tested showed differential sensitivity to PAN and that cultivars resistant to PAN were also resistant to other pollutants. In contrast, studies by Hanson et al. (1976) at Arcadia, CA, found that petunia cultivars (49 siblings from complete diallele crosses of seven commercial lines) sensitive to PAN (sensitivity based on foliar injury intensity) were not necessarily sensitive to O_3. The results from ambient air studies were confirmed by controlled exposures to known PAN concentrations (86 or 120 ppb for 1, 1.5, 2, or 2.5 hr). DeVos et al. (1980) used inbred parents of White Cascade, a PAN-sensitive F_1 hybrid, and Coral Magic, a PAN-tolerant hybrid, to study inheritance of PAN tolerance. Plants were exposed to 150 ppb PAN for 1.5 hr in controlled environment chambers.

Significant genetic variation in breeding lines was detected, but there was also a large genotype-by-environment interaction. Starkey et al. (1976) exposed 10 varieties of bean for 2 hr to 120 or 150 ppb PAN to observe the injury symptomology and to determine differential cultivar sensitivity. All cultivars developed some abaxial bronzing and glazing; only the intensity of symptom expression and the time for symptom development varied among cultivars. The authors compared their ranking of relative PAN sensitivity with published information on O_3 sensitivity for the same cultivars and found that the PAN-sensitive cultivars were not necessarily sensitive to O_3.

Middleton et al. (1950) first described smog injury (PAN type) and listed endive, lettuce, romaine lettuce, and spinach as extremely sensitive but carrot and members of the cabbage and melon families as tolerant. This general ranking of sensitivity is still accepted for PAN. Specific cultivars of petunia, bean, Swiss chard, oats, and cos lettuce were selected for their PAN sensitivity as demonstrated in controlled fumigation studies. Tomato was originally listed as only slightly sensitive to smog (PAN), but it is now known that many varieties are highly sensitive.

Sensitive plants show a characteristic pattern of injury when they are exposed to PAN. As described from field observations in Los Angeles County, CA, by Noble (1955), Juhren et al. (1957), and Glater et al. (1962), leaves of different ages show damage in different positions. A similar description of PAN injury confirms that susceptibility is related to specific physiological stage and foliage development (Taylor, 1969; Taylor and MacLean, 1970; Noble, 1955; and Glater et al., 1962); but the causal factors involved in this selective sensitivity phenomenon have not been identified.

6.6.2.2 Physical Factors. The light-exposure regime to which plants are subjected before, during, and after exposure to phytotoxic concentrations of PAN will significantly affect response (Taylor et al., 1961). Brief dark periods preceding exposure and immediately following exposure can reduce or even prevent the development of visible symptoms of injury. Maximum injury occurs when plants are exposed in full sunlight. Dugger et al. (1963) determined that the maximum quantum responsivity to PAN occurred in the 420 to 480 nm range.

Juhren et al. (1957) found that plants were most susceptible to oxidant injury (PAN-type symptoms) when grown under 8 hr photoperiods, but that injury decreased with photoperiods of 12 to 16 hr. This observation may help to explain why symptoms of PAN injury are most prominent in late fall, winter, and spring in southern California. Juhren also found that the greatest oxidant injury occurred at temperatures of 25° in the daytime and 20°C at night.

The effects of relative humidity, air temperature, and edaphic factors have not been investigated extensively, but some observations have been reported. There is no cohesive evidence regarding the significance of relative humidity and plant susceptibility, but PAN injury to vegetation in the South Coast Air Basin of California occurs most frequently when relative humidity is 50 percent or greater (Taylor, 1974).

Field observations in southern California, where irrigation is essential for crop production, revealed that crops growing under a soil moisture deficit, a period when stomatal conductance is frequently reduced, developed few or no O_3 or PAN-type injury symptoms during a severe smog attack; while adjacent, recently irrigated crops were severely injured (Taylor, 1974). Similarly, the author observed increased tolerance of beans and tobacco to O_3 and PAN when potted test plants were inadvertently allowed to wilt briefly during the day preceding fumigation, even though the plants were watered several hours before treatment and appeared to be normal.

6.6.2.3 Chemical Factors.

6.6.2.3.1 Chemical Additives. The effectiveness of chemical additives applied for pest control, as well as specifically for the prevention of oxidant air pollutant injury, has been studied by Freebairn and Taylor (1960), Pell (1976), and Pell and Gardner (1975, 1979). These studies were designed to determine if cultural practices could be modified to mediate the effects of PAN and other oxidant air pollutants. None of the chemical treatments proved sufficiently effective, however, in preventing or reducing PAN injury to encourage general use.

6.6.2.3.2 Pollutant interactions. The importance of O_3 as a phytotoxicant was not recognized before the 1960s, although it was identified as a major chemical component of the photochemical oxidant complex in the 1950s. It is known that PAN is rarely, if ever, present in the absence of O_3 in photochemically polluted atmospheres (Oshima et al., 1974; Penkett et al., 1977; U.S. Environmental Protection Agency, 1978; Tilton and Bruce, 1981). The ratio of O_3 to PAN in southern California has been reported to be about 10:1 (Taylor, 1969); at Calgary, Canada, the ratio found varied according to atmospheric conditions (Peake and Sandhu, 1983). (See Chapter 5 for a discussion of O_3-to-PAN ratios.)

Interactions involving plant exposure to mixtures of PAN and O_3 in polluted atmospheres probably occur, but the few published reports of controlled

PAN plus O_3 interaction studies with plants have shown variable and inconsistent effects on symptom type and intensity of injury. Kohut et al. (1976) found that O_3 (0.18 ppm) plus PAN (0.18 ppm) treatments for 4 hr in midday produced O_3-type symptoms on hybrid poplar seedlings, but that the amount of injury was highly variable. Davis (1977) found that ponderosa pine seedlings that were exposed to an O_3 (0.40 ppm) plus PAN (0.20 ppm) combination for 4 hr developed significantly less injury than those exposed to O_3 alone. Kohut and Davis (1978) reported greater-than-additive O_3-type injury on bean leaves exposed to the O_3 (0.30 ppm) plus PAN (0.05 ppm) combination for 4 hr, but PAN injury was almost completely suppressed. In a study of the protective effects of benomyl on bean plants exposed to 0.25 ppm O_3 and 0.15 ppm PAN for 3 hr, Pell (1976) found that the combination of O_3 and PAN produced more injury than PAN alone.

Posthumus (1977) exposed little-leaf nettle and annual bluegrass to O_3 (0.17 ppm) and PAN (0.05 ppm) singly and in combination for 2 hr in either the morning or afternoon. The combination induced more foliar injury in the morning than in the afternoon. There was no clear increase or decrease, however, in the foliar injury in the plants exposed to the combination compared to the injury from the single gases. More recent studies with little-leaf nettle (Tonneijck, 1984) showed that no interaction between O_3 and PAN was detected when both were applied at their respective injury threshold concentrations. The pollutant combination caused less than additive injury, however, when the PAN concentration exceeded the injury threshold concentration. Matsushima (1971) studied the effects of SO_2 and PAN, singly and in combination (alternating or in concurrent mixtures), on pinto beans (PAN, 0.45 ppm; SO_2, 1.5 ppm for 90 min), pepper (PAN, 0.37 ppm; SO_2, 2.1 ppm for 70 min) and tomato (PAN 0.40 ppm; SO_2, 1.8 ppm for 60 min). The resultant foliar injury was additive or less than additive from the combination of pollutants. In the mixture, PAN injury tended to appear on the young leaves and SO_2 injury on the mature leaves. Nouchi et al. (1984) exposed petunia and bean plants for 4 hr to mixtures of O_3 and PAN to assess effects on visible symptoms of injury. Ozone concentrations for the petunia study were 0, 0.10, 0.20, 0.30, and 0.40 ppm and PAN concentrations were 0.01, 0.02, 0.03, and 0.04 ppm. In the bean study, O_3 concentrations were 0, 0.15, 0.20, 0.30, and 0.40 ppm, and PAN concentrations were 0, 0.030, 0.045, 0.065, 0.085, and 0.100 ppm. For PAN alone, injury symptoms appeared on petunia at 0.020 ppm PAN; and with bean, injury appeared at 0.030 ppm PAN. The percentage of foliar injury was greatest when plants were exposed to PAN alone, and the percentage injury decreased as the O_3 concentration increased. Temple (1982) exposed four cultivars of tomato plants to PAN-O_3 mixtures (0, 0.025, and 0.050 ppm PAN and 0, 0.10, and 0.20 ppm O_3) for 4 hr once a week for 3 wk. The effects of the mixture on leaf area and leaf dry weight were less than additive. Stomatal conductance was reduced to a greater extent from the mixture than the individual gases.

6.7 PAN EXPOSURE AND RESPONSE

Initial PAN-injury symptoms, which fully develop during the 24 to 72 hr following exposure, are a glazed, bronzed, or metallic sheen on the lower (abaxial) leaf surface. These symptoms are clearly distinct from those produced by O_3, which typically causes upper surface necrotic stipple, fleck chlorosis, or bifacial necrosis on sensitive species (Temple, 1982). Transverse bands of bleached, necrotic tissue and glaze and bronze on the lower surface (Noble, 1955) are characteristic of the PAN injury syndrome (Taylor, 1969). Most sensitive plant species develop diffuse transverse bands of injury in regions where the tissue is in identical stages of physiological development (Figure 6-23). This phenomenon results in injury at the apex of the youngest susceptible leaf and at regions nearer the base of the next successively older three or four leaves. Exposure on successive days results in a series of two or more injured bands separated by bands of healthy tissue, demonstrating that the stage of high susceptibility lasts for only a relatively short period (Noble, 1965). Some leaves, such as the two primary leaves on bean plants, do not develop the bands; the injury may be distributed at random or as a solid cover over the entire lower surface.

Ordin and Propst (1962) demonstrated that the auxin indole acetic acid (IAA) in oat coleoptiles was completely inactivated when 1.3 ppm PAN was passed through the solution in which they were suspended for 3 hr. Similarly, enzyme activity was inhibited by exposures to 1 ppm PAN for 1 hr (Ordin et al., 1971) and to 125 ppm for 6 min (Mudd, 1963). Thomson et al. (1965) found that exposure to 1 ppm PAN for 30 min damaged leaves of pinto bean and chloroplasts were markedly altered as the damage developed. The cell membranes were disrupted and the cell contents clumped together in a large mass. Dugger et al. (1965) reported that PAN inhibited ATP and NADPH formation and the fixation of $^{14}CO_2$, thus inhibiting the photosynthesis of carbohydrates. Coulson and Heath (1975) found that PAN inhibited photosynthesis and that

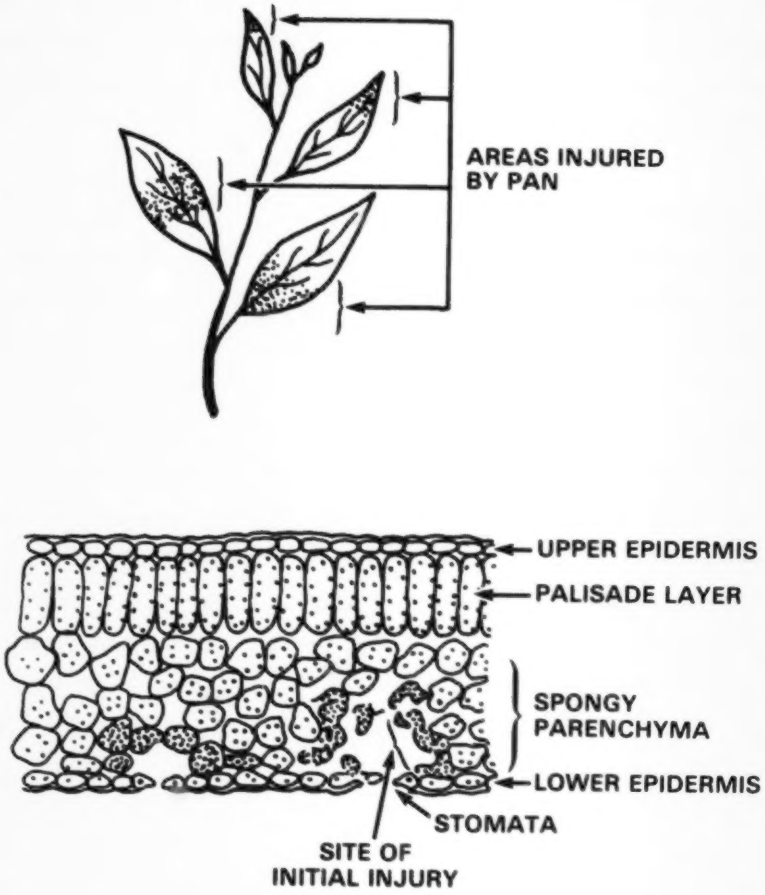
AREAS INJURED BY PAN
UPPER EPIDERMIS
PALISADE LAYER
SPONGY PARENCHYMA
LOWER EPIDERMIS
STOMATA
SITE OF INITIAL INJURY

Figure 6-23. PAN injury. Note position effect with age of leaf. Initial collapse is in the region of a stomate.

Source: Brandt (1962).

photosystems I and II were both affected to a similar extent. These biochemical and physiological studies were conducted with high concentrations of PAN (1 ppm and above) that far exceed those found in the atmosphere, but they demonstrate that reactions essential for plant growth and development may be inhibited.

The response of plants to PAN was summarized in the previous criteria document for ozone and other photochemical oxidants published in 1978 (U.S. Environmental Protection Agency, 1978). Figure 6-24 graphically presents the estimated limiting values for PAN injury as calculated by Jacobson (1977) and presented by the U.S. Environmental Protection Agency (1978). Sensitive plants exposed to doses in the region below and to the left of the data points have a low risk for development of visible injury symptoms. Those plants exposed to doses to the right and above the line are at greater risk of developing injury symptoms. This illustration was based on a limited amount of information and the data were produced by controlled fumigations with synthesized PAN. Plants growing and exposed under ambient field conditions may be at greater risk than indicated by the illustration (see Section 6.6).

In summary, PAN is one member of a family of highly phytotoxic, gaseous compounds in the photochemical oxidant complex. Acute responses of plants to O_3 and PAN result from disruption of normal cell structure and processes. The biochemical and physiological effects of PAN are not understood as well as the effects of O_3. Effects of PAN on plant growth and yield were recognized in the previous criteria document (U.S. Environmental Protection Agency, 1978), but the documented responses were associated with visible injury symptoms. The concept of limiting values (i.e., those concentrations below which foliar injury and, presumably, reduced growth and yield would not occur) was used to illustrate potentially harmful exposures. The range of limiting values for PAN was: 1000 $\mu g/m^3$ (200 ppb) for 0.5 hr; 500 $\mu g/m^3$ (100 ppb) for 1 hr; and 175 $\mu g/m^3$ (35 ppb) for 4 hr. Studies using little-leaf nettle have shown, however, that the limiting values proposed by Jacobson (1977) were insufficient to protect that species from PAN injury (Tonneijck, 1984). In this species, the limiting values would need to be reduced 30 to 40 percent to prevent foliar injury.

Although supporting data for growth and yield response to PAN exposures are deficient, it must be emphasized that yield and growth effects can occur with and without extensive visible symptom development on exposed plants. This section has focused on yield loss as described in Section 6.2. Foliar

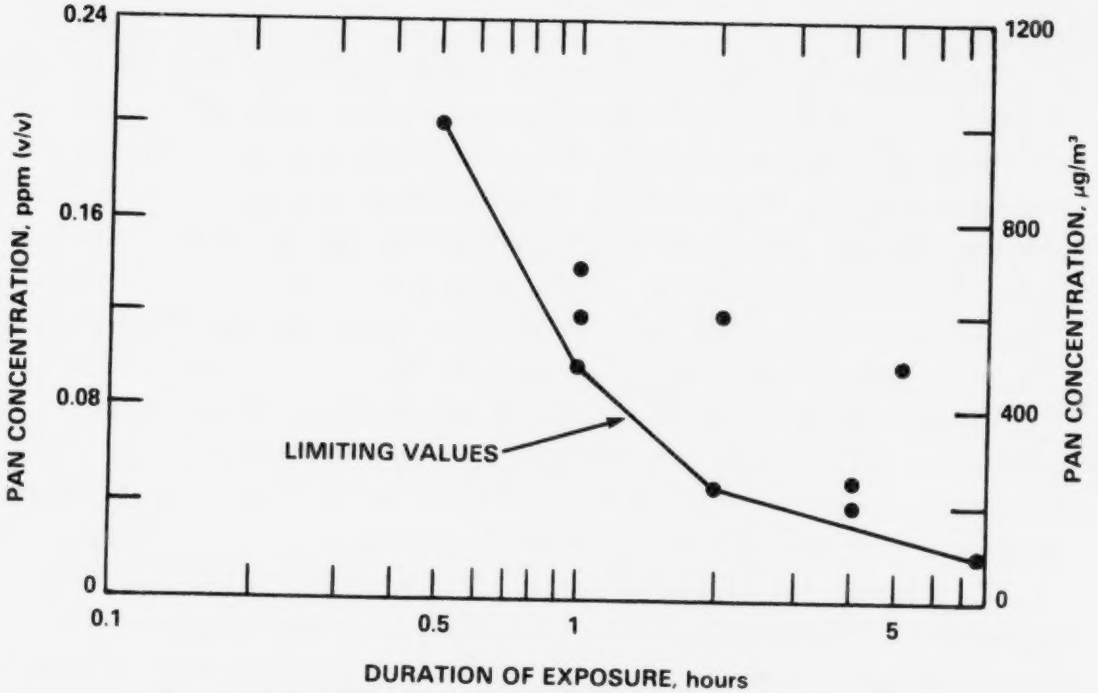

Figure 6-24. Dose-response relationships and limiting values for foliar injury to vegetation by peroxyacetylnitrate (PAN).

Source: U.S. Environmental Protection Agency (1978).

injury is an important factor as a bioindicator of exposure to PAN (see Section 6.7.1 below) and a cause of yield loss as reported periodically in southern California during the past 30 years.

6.7.1 Bioindicators of PAN Exposure

Foliar injury symptoms frequently reduce market value seriously and, in some instances, render the product unmarketable. These symptoms also may destroy a significant amount of photosynthetically active leaf tissue. The injury-symptom syndrome can serve as a very important indicator that damaging PAN exposures have occurred, although it should be noted that the effect may be considerably greater than the actual tissue destruction observed.

The concept of using bioindicators to assess the impact of air pollutants and the methodology involved are presented in Section 6.4.1. The PAN injury symptoms that are most useful in field diagnosis are the diffuse transverse bands of injury, which may be visible only on the lower leaf surface or on both surfaces; and the glazing, silvering, bronzing, or metallic sheen, or all of these, on the lower leaf surface. Recognition of PAN injury in the field is not always a simple process because a type of lower leaf surface glaze and bronze may be produced by other factors such as cold temperatures, insects (mites), and other air pollutants: O_3, hydrochloric acid (HCl), SO_2, and hydrofluoric acid (HF). In making field assessments, it is important that the observer know the relative susceptibility of the crop and the native and ornamental species in the area and that as many different species as possible be examined.

Noble (1965) reported on a 6-yr study in southern California designed to use plant indicators to identify injury induced by air pollutants. He used six agricultural crops and two weed species widely distributed in the area. The study revealed that annual blue grass (meadowgrass) was a very good indicator for PAN. Posthumus (1977) found that little-leaf nettle and annual bluegrass developed characteristic PAN-type injury symptoms when exposed to about 50 ppb (0.05 ppm) PAN, and he suggested that these wild species might be accurate indicators. Sawada et al. (1974) used 16 plant species in a survey for O_3 and PAN injury and observed PAN injury on 28 percent of the 138 plants used in the study.

Field surveys in southwestern Ontario, Canada (Pearson et al., 1974) revealed PAN-type injury symptoms on tomato crops. On the basis of these symptoms and the meteorological conditions that occurred during their development, the authors concluded that the air pollutants probably originated in the Cleveland, OH, area. Bioindicators should be used cautiously, however, when monitoring data are not available to verify PAN concentrations and when observations are made on a single plant species. Lewis and Brennan (1978) reported PAN-type injury on petunia leaves exposed to mixtures of O_3 and SO_2. Wood and Drummond (1974) suggested that PAN-type injury may be caused by interactions of PAN and other phytotoxicants or perhaps by a single pollutant such as HCl.

Field observations and diagnosis provide an important means of determining if a PAN problem exists. Although PAN can be measured chromatographically, the instrument can be calibrated only with known concentrations of PAN. The problems associated with the synthesis, dilution, and measurement of PAN for calibration purposes have discouraged the establishment of monitors for long-term use (see Chapter 4). Plant-damaging exposures of PAN have been verified with monitoring instrumentation in only a very few locations. Therefore, the ability to recognize and evaluate PAN injury symptoms in the field is very important.

Foliar injury of the type induced by PAN has been reported in more than half of the counties in California, in several states, and in several foreign countries. Went (1955) reported PAN-type injury in some European and South American cities as well as in several cities in the eastern United States. Locations at which PAN injury was observed on vegetation in the United States are presented in Table 6-33.

6.7.2 Nonvascular Plant Response to PAN Exposure

Gross and Dugger (1969) examined the effects of PAN on algae (*Chlamydomonas reinhardtii*) by measuring growth, photosynthesis, respiration, and pigment content of the cells. Treatment usually lasted for several minutes, during which PAN was bubbled through a liquid medium containing the algal cells. The gaseous mixture usually contained an average PAN concentration of 125 ppm in nitrogen (N_2), with the treatment dose expressed in nanomoles (nM). Exposures ranged from 20 to 250 nM. The study results indicated that both autotrophic and heterotrophic growth was inhibited, photosynthesis and respiration were adversely affected, and photosynthesis was more severely affected than respiration. The results also indicated that carotenoids were destroyed and that there was destruction of both chlorophylls, although chlorophyll *a* was more stable than chlorophyll b. Gross and Dugger (1969) also reported that PAN lowered the free sulfhydryl content (-SH) of the cells.

Field studies of the lichen populations in the southern California mountains indicated trends in ecosystem community parameters that inferred that oxidant air pollutants had a deleterious effect on lichens (Sigal and Taylor, 1979). They fumigated three species for 4 hr/day for 8 days with 50 ppb PAN. In one experiment, the lichens were fumigated for only 7 days with 0.100 ppm PAN. Photosynthesis was inhibited in Parmelia sulcata, probably inhibited in Hypogymnia entermospha (results were highly variable), and appeared not to be affected in Collema nigrescens. The difference in gross response of photosynthesis to PAN fumigations exhibited by these three lichen species tends to indicate that PAN, along with other pollutants, may be detrimental to lichen populations.

6.7.3 Losses in Vascular Plants Caused by PAN

The term loss is used in this section to mean loss in the intended use or value of vegetation caused by PAN injury. The loss may be a reduction in amount of marketable product or a loss resulting from aesthetic degradation.

6.7.3.1 Losses in Aesthetic Use and Foliar Yield. Petunias, a species highly susceptible to PAN injury, are frequently used as bedding plants. Although monetary losses from PAN injury to vegetation have not been studied, it is obvious that they can occur, affecting the wholesale industry, retail market, and the consumer (e.g., in the Los Angeles Basin, CA). Although such information is not reported in the literature (O.C. Taylor, personal communication), attempts have been made to produce plants outside heavily polluted areas and transport them to the market. This practice was only partly successful because substantial foliar injury usually developed after delivery to retail outlets and before retail sale. While the petunia is one of the most susceptible species, other ornamentals that are planted for foliage and blossoms also are affected.

Several vegetable crops such as leaf lettuce, spinach, mustard greens, table beets, endive, and romaine lettuce are grown and marketed for their foliage. Some of these crops are grown in close proximity to metropolitan areas and marketed as specialty crops. These species are harvested early in the morning and are supplied, at relatively high prices, to restaurants and specialty stores. After a heavy PAN attack, entire crops in some areas are not marketable, and others require expensive hand work to sort and trim the product to make them acceptable. No reliable assessment of such losses has been made, but losses of several hundred thousand dollars per year in the Los Angeles, CA, area have been suggested (Middleton et al., 1950, 1956).

The indirect effect of PAN on plant growth resulting from destruction of leaf tissue has not been measured. Destruction, however, of a significant amount of leaf area caused by the necrotic bands, damage to the lower epidermis, and increased defoliation of deciduous plants should be expected to suppress growth. Earlier reports indicated that growth and yield by most plants are not measurably affected until the loss of photosynthetic surface exceeds 5 percent (Thomas and Hendricks, 1956). Plants that rapidly replace foliage (e.g., grasses) might be expected to express less growth reduction because of foliage loss than plants that retain their foliage for several years (e.g., citrus trees) and replace the lost foliage more slowly.

Thompson and Kats (1975) reported a trend toward reduced yield of mature navel orange fruit when branches of mature trees were enclosed and fumigated with PAN dosages equivalent to those occurring in the Riverside, CA, area. The treatments consisted of carbon-filtered air, ambient air, and carbon-filtered air plus additions of PAN adjusted to simulate concentrations monitored in the ambient air at Riverside. The continuous treatments were administered for 9 months. Tree growth was suppressed, presumably because of lost photosynthetically active tissue when leaf drop was stimulated.

6.7.3.2 Losses Determined by PAN Addition Studies. Based on PAN addition studies using several species, Temple (1982) concluded that the potentially phytotoxic episodes could be defined as concentrations greater than 15 ppb (0.015 ppm) for 4 hr in the morning or greater than 25 ppb for 4 hr in the afternoon. His experiments were conducted in Teflon®-covered CSTR chambers in a greenhouse. Concentrations of approximately 14 ppb PAN for 4 hr in ambient air are sufficient to produce foliar injury on susceptible plants growing in the field (Taylor, 1969). In chamber studies, however, approximately two to three times this dose was required to induce injury symptoms (Posthumus, 1977). Because of this discrepancy between chamber and field studies, it is difficult to relate responses obtained in chambers using synthesized PAN to responses expected in the field.

Greenhouse exposures of lettuce and Swiss chard to 0, 25, and 50 ppb PAN for 4 hr/day once a week for up to 4 wk caused no visible leaf injury and appeared to have little, if any, effect on plant growth (Temple, 1982). By itself, or in combination with O_3, PAN had no effect on stomatal conductance.

Temple (1982) found that PAN and O_3 alone and in combination reduced growth in four tomato varieties and altered partitioning of photosynthate between roots and shoots. He exposed the plants to 0, 0.1, and 0.2 ppm O_3 and 0, 0.025, and 0.050 ppm PAN, alone and in all combinations, for 4 hr/day once a wk for 3 wk. No PAN-type visible injury developed on the tomato plants and this exposure had no effect on expression of O_3 injury. The PAN treatments had no effect on stomatal conductance, but 0.2 ppm O_3 reduced stomatal conductance in all four varieties. Results from two separate experiments were erratic, perhaps because the studies were conducted at different times of the year. The evidence that the root/shoot ratio was altered suggests, however, that further study is needed.

Greenhouse-grown plants (radish, lettuce, chard, oat, tomato, pinto bean, beet, and barley) representing root, foliage, fruit and seed crops were exposed to PAN (0, 0.005, 0.010, 0.020, or 0.040 ppm) for 4 hr/day, twice per wk from germination to maturity of the harvestable crop (Taylor et al., 1983). Significant yield reductions were observed only in lettuce (Empire) and chard; the threshold for yield reduction appeared to be between 0.010 and 0.020 ppb. Yield was reduced 13 percent in lettuce and 23 percent in chard exposed to 40 ppb. Of all the crops tested, only pinto bean developed a significant amount of foliar injury and only after exposure to 0.040 ppb; this sensitivity persisted throughout the developmental cycle of the crop. The results indicate that PAN at concentrations below the visible injury threshold can cause significant yield reductions in sensitive cultivars of leafy (foliage) crops.

Field observations in southern California during the past 30 years have revealed that severe visible PAN injury seldom appears during mid-summer, even though higher dosages and concentrations occur during the four summer months (Temple and Taylor, 1983). Ozone dosage also is highest during this period. To assess effectively the impact of PAN, in the presence and absence of visible symptoms, experiments should be designed to use O_3 and PAN mixtures, be conducted in as near full sunlight as possible, and be able to simulate fall and spring environmental conditions limited to those periods.

Youngner and Nudge (1980) measured the relative susceptibility of cultivars of 10 turfgrass species exposed to 0.050 ppm PAN or to 0.5 ppm O_3 for 3 hr. They reported a significant variation in amounts of foliar injury and noted that warm-season grasses were more tolerant of both O_3 and PAN than were the cool-season grasses.

Evidence of plant growth suppression following intermittent exposure to PAN at concentrations comparable to those found in ambient polluted air without visible leaf injury symptoms has been reported (Thompson and Kats, 1975; Temple, 1982).

6.8 SUMMARY

Foliar injury on vegetation is one of the earliest and most obvious manifestations of O_3 injury. The effects of O_3 are not limited to visible injury, however. Impacts can range from reduced plant growth and decreased yield, to changes in crop quality and alterations in susceptibility to abiotic and biotic stresses. The plant foliage is the primary site of O_3 effects, although significant secondary effects, including reduced growth (both roots and foliage) and yield, can occur.

Ozone exerts a phytotoxic effect only if a sufficient amount reaches the sensitive cellular sites within the leaf. The O_3 diffuses from the ambient air into the leaf through the stomata, which can exert some control on O_3 uptake, to the active sites within the leaf. Ozone injury will not occur if (1) the rate of O_3 uptake is low enough that the plant can detoxify or metabolize O_3 or its metabolites; or (2) the plant is able to repair or compensate for the effects (Tingey and Taylor, 1982). This is analogous to the plant response to SO_2 (Thomas et al., 1950). Cellular disturbances that are not repaired or compensated are ultimately expressed as visible injury to the leaf or as secondary effects that can be expressed as reduced root growth, or reduced yield of fruits or seeds, or both.

Plant growth and yield are the end products of a series of biochemical and physiological processes related to uptake, assimilation, biosynthesis, and translocation. Sunlight drives the processes that convert carbon dioxide into the organic compounds (assimilation) necessary for plant growth and development. In addition to nutrients supplied through photosynthesis, the plant must extract from the soil the essential mineral nutrients and water for plant growth. Plant organs convert these raw materials into a wide array of compounds required for plant growth and yield. A disruption or reduction in the rates of uptake, assimilation, or subsequent biochemical reactions will be reflected in reduced plant growth and yield. Ozone would be expected to reduce plant growth or yield if (1) it directly impacted the plant process that was limiting plant growth; or (2) it impacted another step sufficiently so that it becomes the step limiting plant growth (Tingey, 1977). Conversely, O_3 will not limit plant growth if the process impacted by O_3 is not or does not become rate-limiting. This implies that not all effects of O_3 on plants are reflected in growth or yield reductions. These conditions also suggest that there are combinations of O_3 concentration and exposure duration that the plant can experience that will not result in visible injury or reduced plant growth and yield. Indeed, numerous studies have demonstrated combinations of concentration and time that did not cause a significant effect on the plant growth or yield.

Ozone induces a diverse range of effects on plants and plant communities. These effects are usually classified as either injury or damage. Injury encompasses all plant reactions such as reversible changes in plant metabolism (e.g., altered photosynthesis), leaf necrosis, altered plant quality, or reduced growth that does not impair yield or the intended use of the plant (Guderian, 1977). In contrast, damage or yield loss includes all effects that reduce or impair the intended use or the value of the plant. Thus, for example, visible foliar injury to ornamental plants, detrimental responses in native species, and reductions in fruit and grain production are all considered damage or yield loss. Although foliar injury is not always classified as damage, its occurrence is an indication that phytotoxic concentrations of O_3 are present. The occurrence of injury indicates that additional studies should be conducted in areas where vegetation shows foliar injury to assess the risk of O_3 to vegetation and to determine if the intended use or value of the plants is being impaired.

6.8.1 Limiting Values of Plant Response to Ozone

Several approaches have been used to estimate the O_3 concentrations and exposure durations that induce foliar injury. Most of these studies used short-term exposures (less than 1 day) and measured visible injury as the response variable. One method for estimating the O_3 concentrations and exposure durations that would induce specific amounts of visible injury involves exposing plants to a range of O_3 concentrations and exposure durations, and then evaluating the data by regression analysis (Heck and Tingey, 1971). The data obtained by this method for several species are summarized in Table 6-34 to illustrate the range of concentrations required to induce foliar injury (5% and 20%) on sensitive, intermediate, and less sensitive species.

TABLE 6-34. OZONE CONCENTRATIONS FOR SHORT-TERM EXPOSURES THAT PRODUCE 5 OR 20 PERCENT INJURY TO VEGETATION GROWN UNDER SENSITIVE CONDITIONS[a]
(ppm)

Exposure time, hr	Ozone concentrations that may produce 5% (20%) injury: Sensitive plants	Intermediate plants	Less sensitive plants
0.5	0.35 - 0.50 (0.45 - 0.60)	0.55 - 0.70 (0.65 - 0.85)	≧0.70 (0.85)
1.0	0.15 - 0.25 (0.20 - 0.35)	0.25 - 0.40 (0.35 - 0.55)	≧0.40 (0.55)
2.0	0.09 - 0.15 (0.12 - 0.25)	0.15 - 0.25 (0.25 - 0.35)	≧0.30 (0.40)
4.0	0.04 - 0.09 (0.10 - 0.15)	0.10 - 0.15 (0.15 - 0.30)	≧0.25 (0.35)
8.0	0.02 - 0.04	0.07 - 0.12	≧0.20 (0.30)

[a] The concentrations in parenthesis are for the 20% injury level.

Source: U.S. Environmental Protection Agency (1978).

An alternative method for estimating the O_3 concentrations and exposure durations that induce foliar injury is the use of the limiting-value approach (Jacobson, 1977). The limiting-value method, which was developed from a review of the literature, identified the lowest concentration and exposure duration reported to cause visible injury on various plant species. The analysis was based on more than 100 studies of agricultural crops and 18 studies of tree species. The analysis yielded the following range of concentrations and exposure durations that were likely to induce foliar injury (U.S. Environmental Protection Agency, 1978):

1. Agricultural crops:
   a. 0.20 to 0.41 ppm for 0.5 hr.
   b. 0.10 to 0.25 ppm for 1.0 hr.
   c. 0.04 to 0.09 ppm for 4.0 hr.
2. Trees and shrubs:
   a. 0.20 to 0.51 ppm for 1.0 hr.
   b. 0.10 to 0.25 ppm for 2.0 hr.
   c. 0.06 to 0.17 ppm for 4.0 hr.

It should be emphasized that both methods described above can estimate concentrations and exposure durations that might induce visible injury, but that neither method can predict impacts of O_3 on crop yield or intended use.

The concept of limiting values also was used to estimate the O_3 concentrations and exposure durations that could potentially reduce plant growth and yield (U.S. Environmental Protection Agency, 1978). The data were analyzed and plotted in a manner similar to the approach used by Jacobson (1977) (Figure 6-25). In Figure 6-25 the line bounds mean O_3 concentrations and exposure durations below which effects on plant growth and yield were not detected. This graphical analysis used data from both greenhouse and field studies and indicated that the lower limit for reduced plant performance was a mean O_3 concentration of 0.05 ppm for several hours per day for exposure periods greater than 16 days. At 10 days the O_3 response threshold increased to about 0.10 ppm, and to about 0.30 ppm at 6 days.

6.8.2 Methods for Determining O_3 Yield Losses

Diverse experimental procedures have been used to study the effects of O_3 on plants, ranging from studies done under highly controlled conditions, to exposures in open-top chambers, and to field exposures without chambers. In general, the more controlled conditions are most appropriate for investigating specific responses and for providing the scientific basis for interpreting and extrapolating results. These systems are powerful tools for adding to an understanding of the biological effects of air pollutants. To assess, however, the impact of O_3 on plant yield and to provide data for economic assessments, deviations from the typical environment in which the plant is grown should be minimized. For field crops, this implies that the studies should be conducted in the field, but for crops that are typically grown in glass houses, the studies should be conducted under glass-house conditions.

To improve estimates of yield loss in the field, the National Crop Loss Assessment Network (NCLAN) was initiated by EPA in 1980 to estimate the magnitude of crop losses caused by O_3 (Heck et al., 1982). The primary objectives of NCLAN were:

1. To define the relationships between yields of major agricultural crops and O_3 exposure as required to provide data necessary for economic assessments and the development of National Ambient Air Quality Standards;

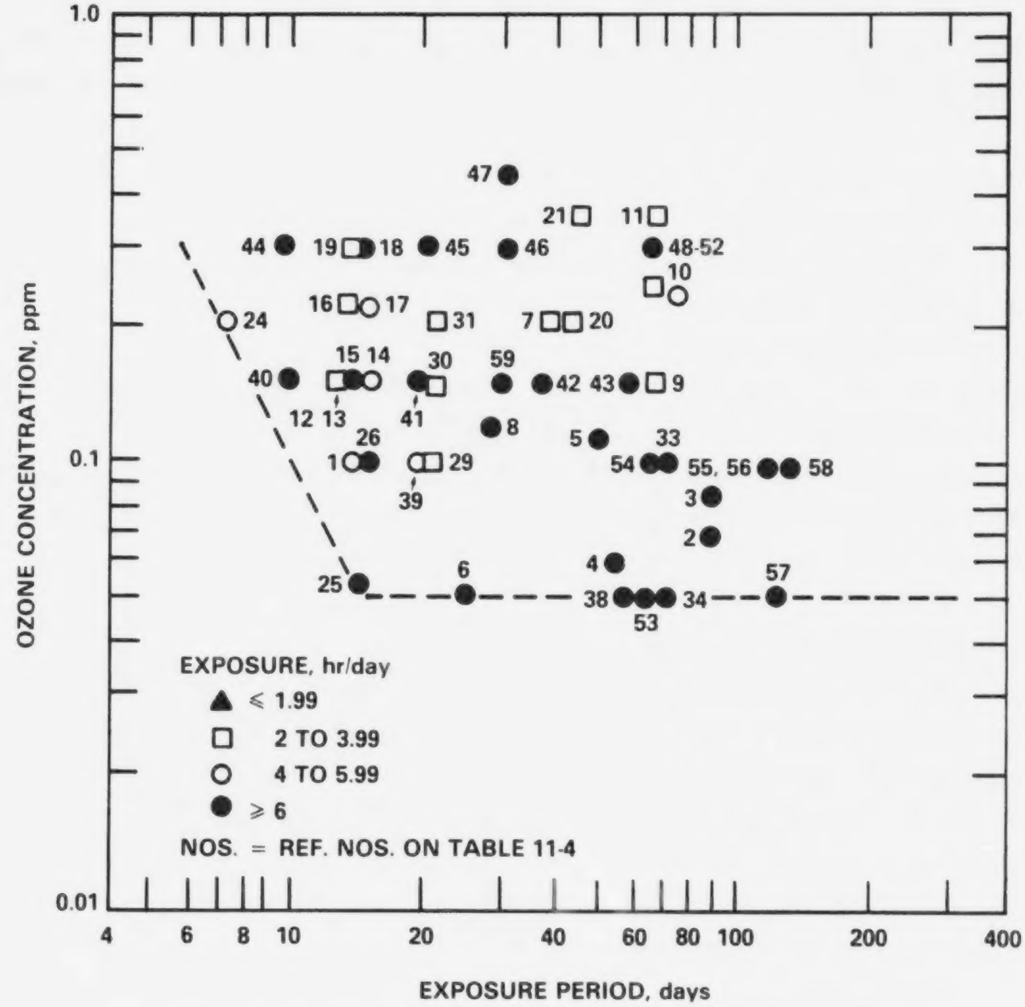

Figure 6-25. Relationship between ozone concentration, exposure duration, and reduction in plant growth or yield (see Table 6-18; also U.S. EPA, 1978).

Source: U.S. Environmental Protection Agency (1978).

2. To assess the national economic consequences resulting from the exposure of major agricultural crops to O_3;
3. To advance understandng of the cause and effect relationships that determine crop responses to pollutant exposures.

In the NCLAN studies, the cultural conditions used approximated typical agronomic practices, and open-top field exposure chambers were used to minimize perturbations to the plant environment during the exposure. The studies have attempted to use a range of realistic O_3 concentrations and sufficient replication to permit the development of exposure-response models. In the NCLAN studies, plants were exposed to a range of O_3 concentrations. Chambers were supplied with either charcoal-filtered air (control), ambient air, or ambient air supplemented with O_3 to provide concentrations three or four levels greater than ambient. Consequently, the O_3 exposures were coupled to the ambient O_3 level; days with the highest ambient O_3 were also the same days when the highest concentrations occurred in a specific treatment in a chamber. As the ambient O_3 varied from day-to-day, the base to which additional O_3 was added also varied. This coupling of the O_3 exposures to the ambient environment means that high O_3 concentrations occurred in the chambers when the environmental and air chemistry conditions, in the ambient air, were conducive for producing elevated ambient O_3 levels. The plant response data have been analyzed using regression approaches. The exposures were typically characterized by a 7-hr (9:00 a.m. to 4:00 p.m.) seasonal mean O_3 concentration. This is the time period when O_3 was added to the exposure chambers.

6.8.3 Estimates of Ozone-Induced Yield Loss

Yield loss is defined as an impairment or decrease in the intended use of the plant. Included in the concept of yield loss are reductions in aesthetic values, the occurrence of foliar injury (changes in plant appearance), and losses in terms of weight, number, or size of the plant part that is harvested. Yield loss may also include changes in physical appearance, chemical composition, or ability to withstand storage; which collectively are traits called crop quality. Losses in aesthetic values are difficult to quantify. For example, because of its aesthetic value, the loss of or adverse effect on a specimen plant in a landscape planting may result in a greater economic loss than that incurred by the same impact on a plant of the same species growing as a part of natural plant community. Foliar injury symptoms may decrease the value of ornamental plants with or without concomitant growth reductions. Similarly, foliar injury on crops in which the foliage is the marketable plant part (e.g., spinach, lettuce, cabbage) can substantially reduce marketability and thus can constitute yield loss. Attainment of the limiting values for ozone previously discussed in this section should be sufficient to prevent foliar injury and thereby reduce this type of yield loss. Most studies of the relationship between yield loss and ozone concentration have focused on yields as measured by weight of the marketable plant organ, and that kind of yield loss will be the primary focus of this section.

Studies have been conducted, frequently using open-top field exposure chambers, to estimate the impact of O_3 on the yield of various crop species. These studies can be grouped into two types, depending on the experimental design and statistical methods used to analyze the data: (1) studies that developed predictive equations relating O_3 exposure to plant response, and (2) studies that compared discrete treatment levels to a control. The advantage of the regression approach is that exposure-response models can be used to interpolate results between treatment levels.

When the regression approach was used to estimate yield loss, O_3 was added to either charcoal-filtered or ambient air to create a range of O_3 concentrations. In summarizing the data, O_3-induced yield loss was derived from a comparison of the performance of the plants in charcoal-filtered air, although other reference concentrations have been used. Various regression techniques have been used to derive exposure-response functions. The use of regression approaches permits the estimation of the O_3 impact on plant yield over the range of concentrations, not just at the treatment means as is the case with analysis of variance methods.

6.8.3.1 Yield-loss: Determination by Regression Analysis. Examples of the relationship between O_3 concentration and plant yield are shown in Figures 6-26 and 6-27. These cultivars and species were selected because they also illustrated the type of year-to-year variation in plant response to ozone that may occur. The derived regression equations can be used to determine the concentrations that would be predicted to cause a specific yield loss or to estimate the predicted yield loss that would result from a specifc O_3 concentration. Both approaches have been used to summarize the data on crop responses to O_3 using the Weibull function (Rawlings and Cure, 1985). As an example of

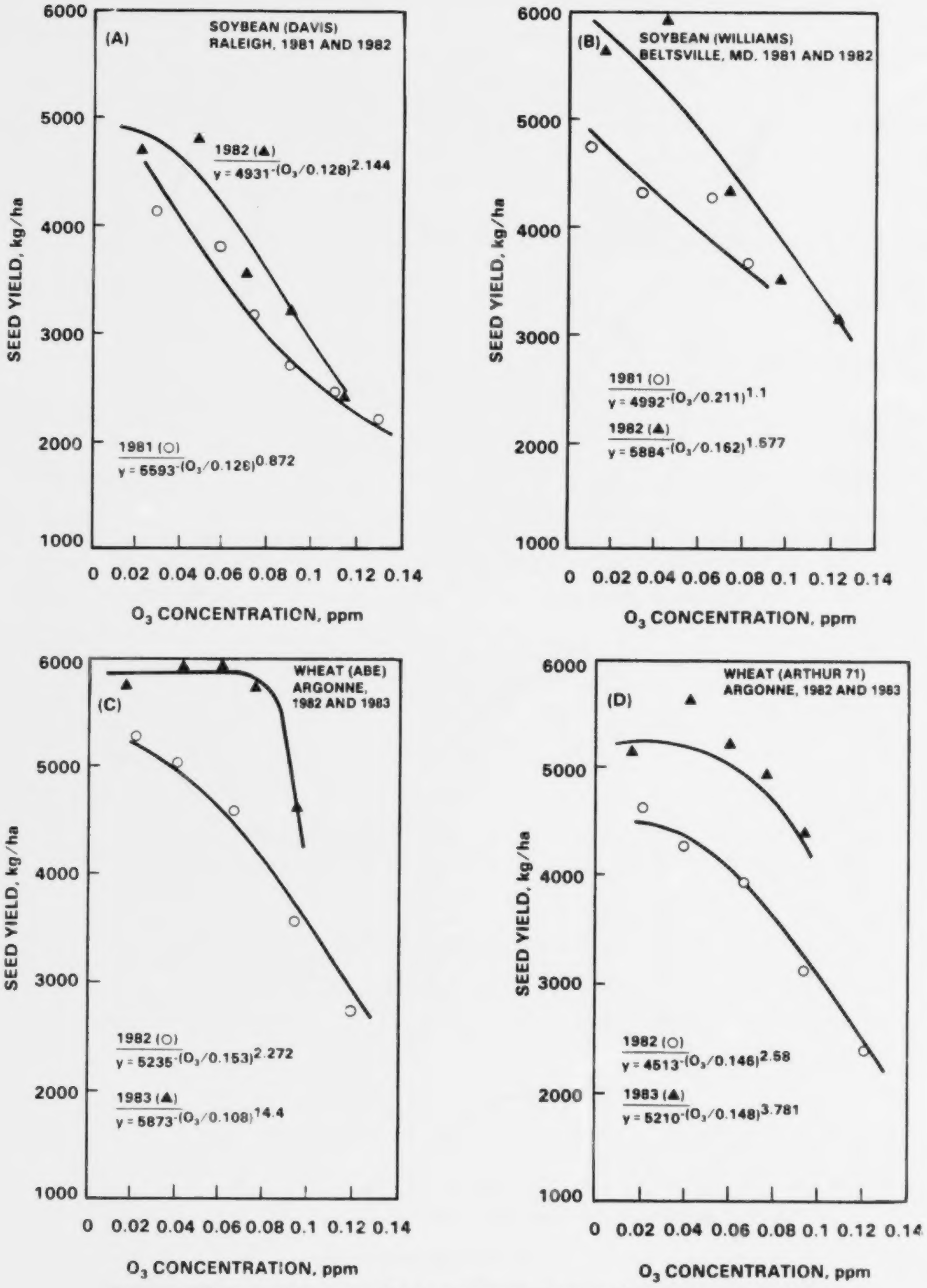

Figure 6-26. Examples of the effects of ozone on the yield of soybean and wheat cultivars. The O_3 concentrations are expressed as 7-hr seasonal mean concentrations. The cultivars were selected as examples of O_3 effects and of year-to-year variations in plant response to O_3.

Source: Soybean data from Heck et al. (1984b); wheat data from Kress et al. (1985).

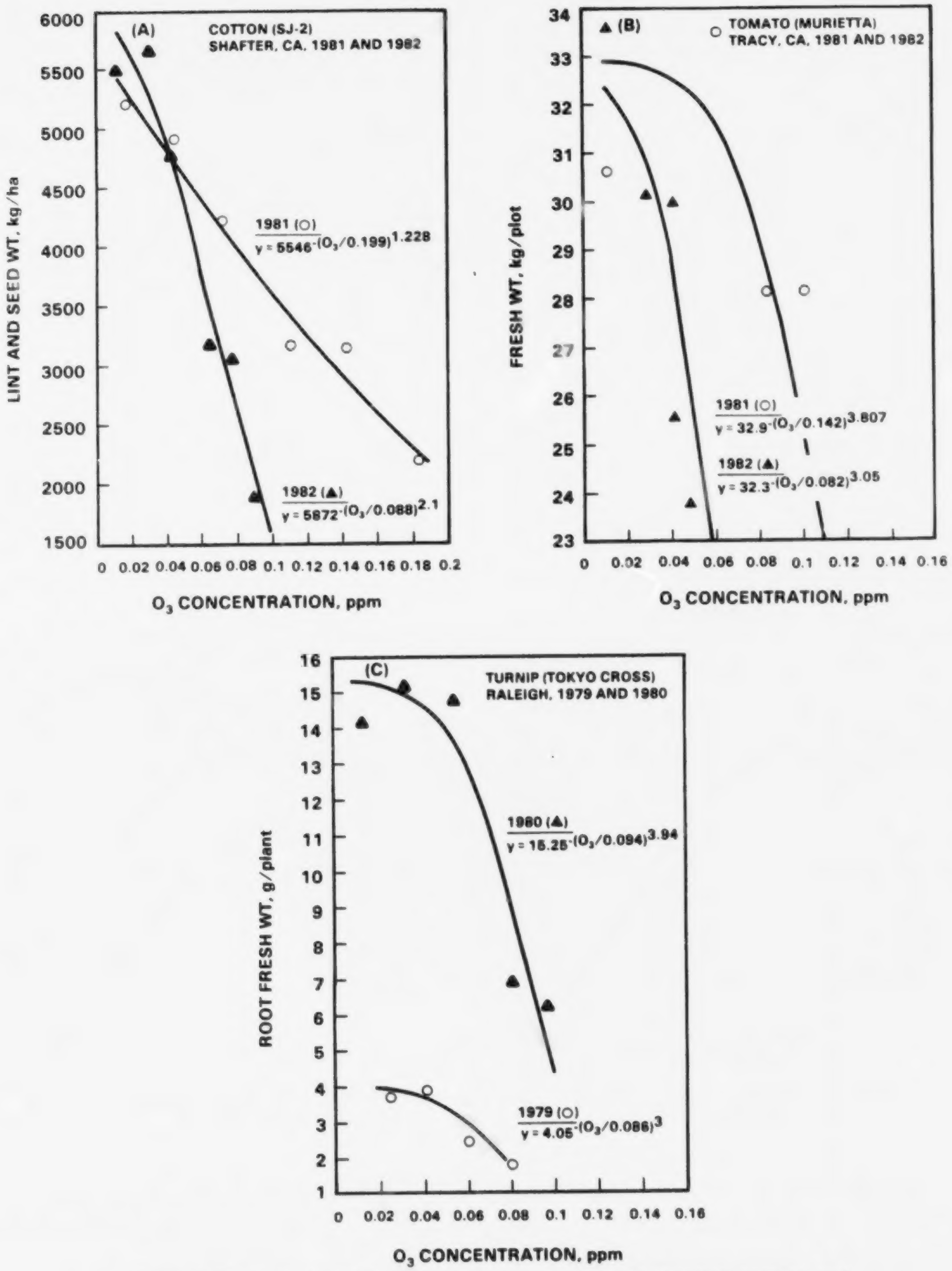

Figure 6-27. Examples of the effects of ozone on the yield of cotton, tomato, and turnip. The O_3 concentrations are expressed as 7-hr seasonal mean concentrations. The species were selected as examples of O_3 effects and of year-to-year variations in plant response to O_3.

Source: Cotton and tomato data from Heck et al. (1984b); turnip data from Heagle et al. (1985).

response, the O_3 concentrations that would be predicted to cause a 10 or 30 percent yield loss have been estimated (Table 6-35). A brief review of the data in this table indicates that for some species mean yield reductions of 10 percent were predicted when the 7-hr seasonal mean O_3 concentration exceeded 0.04 to 0.05 ppm. Concentrations of 0.028 to 0.033 ppm were predicted to cause a 10 percent yield loss in Vona wheat, kidney bean, and Hodgson soybean. At a 7-hr seasonal mean O_3 concentration of 0.04 ppm, mean yield reductions ranged from zero percent in sorghum, barley, and a corn cultivar to a high of 28.8 percent in Vona wheat.

A histogram of the 7-hr seasonal mean O_3 concentrations predicted to cause a 10 percent yield loss (Table 6-35) is given in Figure 6-28 to help illustrate the range of concentrations and their relative frequency of occurrence. The data in Figure 6-28 are based on 37 species or cultivar yield-response functions developed from studies in open-top field exposure chambers. Approximately 57 percent of the species or cultivars were predicted to exhibit 10 percent yield reductions at 7-hr seasonal mean concentrations below 0.05 ppm. Thirty-five percent of plant types were predicted to display a 10 percent yield loss at 7-hr mean concentrations between 0.04 and 0.05 ppm. Seven-hr seasonal mean concentrations in excess of 0.08 ppm were required to cause a 10 percent yield loss in almost 19 percent of the species or cultivars. The data indicate that approximately 11 percent of the species or cultivars would display a 10 percent loss at 7-hr seasonal mean concentrations below 0.035 ppm, suggesting that these plant types are very sensitive to O_3-induced yield losses.

A review of the data in Table 6-35 indicates that the grain crops were apparently generally less sensitive than the other crops to O_3. Mean yield reductions at 0.04 ppm were predicted to be less than 5 percent for all the species and cultivars tested except for the Roland and Vona wheat cultivars. The data also demonstrate that sensitivity differences within a species may be as large as differences between species. For example, at 0.04 ppm O_3, estimated yield losses ranged from 2 to 15 percent in soybean and from 0 to 28 percent in wheat. In addition to differences in sensitivity among species and cultivars, the data in Figures 6-26 and 6-27 illustrate year-to-year variations in plant response to O_3.

Several exposure-response models, ranging from simple linear to complex nonlinear models, have been used to describe the relationship between plant yield and O_3 exposure. When exposure-response models are used, it is important

TABLE 6-35. SUMMARY OF OZONE CONCENTRATIONS PREDICTED TO CAUSE 10 PERCENT AND 30 PERCENT YIELD LOSSES AND SUMMARY OF YIELD LOSSES PREDICTED TO OCCUR AT 7-hr SEASONABLE MEAN OZONE CONCENTRATIONS OF 0.04 and 0.06 ppm[a]

	O_3 concentrations, ppm, predicted to cause yield losses of:		Percent yield losses predicted to occur at 7-hr seasonal mean O_3 concentration of:	
Species	10%	30%	0.04 ppm	0.06 ppm
Legume crops				
Soybean, Corsoy	0.048	0.082	6.4	16.6
Soybean, Davis (81)	0.038	0.071	11.5	24.1
Soybean, Davis (CA-82)	0.048	0.081	6.4	16.5
Soybean, Davis (PA-82)	0.059	0.081	2.0	10.4
Soybean, Essex	0.048	0.099	7.2	14.3
Soybean, Forrest	0.076	0.118	1.7	5.3
Soybean, Williams	0.039	0.093	10.4	18.1
Soybean, Hodgson	0.032	0.066	15.4	18.4
Bean, Kidney	0.033	0.063	14.9	28
Peanut, NC-6	0.046	0.073	6.4	19.4
Grain crops				
Wheat, Abe	0.059	0.095	3.3	10.4
Wheat, Arthur 71	0.056	0.094	4.1	11.7
Wheat, Roland	0.039	0.067	10.3	24.5
Wheat, Vona	0.028	0.041	28.8	51.2
Wheat, Blueboy II	0.088	0.127	0.5	2.8
Wheat, Coker 47-27	0.064	0.107	2.2	8.4
Wheat, Holly	0.099	0.127	0.0	0.9
Wheat, Oasis	0.093	0.135	0.4	2.4
Corn, PAG 397	0.095	0.126	0.3	1.5
Corn, Pioneer 3780	0.075	0.111	1.4	5.1
Corn, Coker 16	0.133	0.175	0.0	0.3
Sorghum, DeKalb-28	0.108	0.186	0.0	2.7
Barley, Poco	0.121	0.161	0.0	0.5
Fiber crops				
Cotton, Acala SJ-2 (81)	0.044	0.096	8.3	16.2
Cotton, Acala SJ-2 (82)	0.032	0.055	16.1	35.1
Cotton, Stoneville	0.047	0.075	4.6	16.2
Horticultural crops				
Tomato, Murrieta (81)	0.079	0.108	0.8	3.7
Tomato, Murrieta (82)	0.040	0.059	10.3	31.2
Lettuce, Empire	0.053	0.075	0.0	16.8
Spinach, America	0.046	0.082	6.8	17.2
Spinach, Hybrid	0.043	0.082	2.6	9.2
Spinach, Viroflay	0.048	0.080	6.0	16.7
Spinach, Winter Bloom	0.049	0.080	5.8	16.5
Turnip, Just Right	0.043	0.064	7.7	24.9
Turnip, Pur Top W. G.	0.040	0.064	10.1	26.5
Turnip, Shogoin	0.036	0.060	13.0	29.7
Turnip, Tokyo Cross	0.053	0.072	3.3	15.6

[a] The yield losses are derived from Weibull equations and are based on the control yields in charcoal-filtered air.

Source: Derived from Heck et al. (1984b).

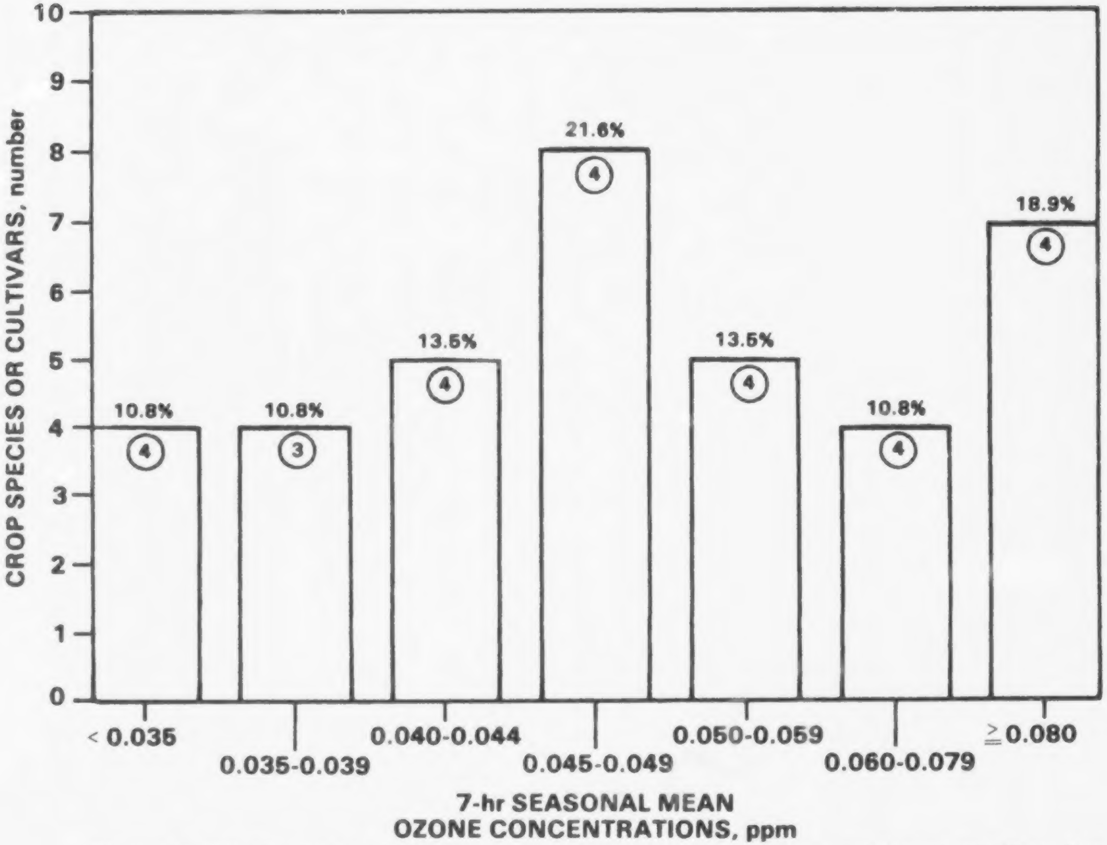

Figure 6-28. Number and percentage of 37 crop species or cultivars predicted to show a 10 percent yield loss at various ranges of 7-hr seasonal mean ozone concentrations. Concentration ranges and 10% yield loss data are derived from Table 6-35. Data represent 12 separate crop species; circled numbers represent separate species for each concentration range.

for the fitted equations not to show systematic deviation from the data points and for the coefficient of determination (R^2) to be high. Although linear regression equations have been used to estimate yield loss, there appear to be systematic deviations from the data for some species and cultivars even though the equations have moderate-to-high coefficients of determination (R^2). Plateau-linear or polynomial equations appear to fit the data better. More recently, a Weibull model has been used to estimate percentage yield loss (Heck et al., 1983a). The Weibull model yields a curvilinear response line that seems to provide a reasonable fit to the data. Based on available data, it is recommended that curvilinear exposure-response functions be used to describe and analyze plant response to O_3.

6.8.3.2 Yield Loss: Determination from Discrete Treatments. In addition to the use of regression approaches in some studies, various other approaches have been used to investigate the effects of O_3 on crop yield. These studies were designed to test whether specific O_3 treatments were different from the control rather than to develop exposure-response equations. In general, these data were analyzed using analysis of variance. To summarize the data from studies that used discrete treatments, the lowest O_3 concentration that significantly reduced yield was determined from analyses done by the authors (Table 6-36). The lowest concentration reported to reduce yield was frequently the lowest concentration used in the study; hence it was not always possible to estimate a no-effect exposure concentration. In general, the data indicate that O_3 concentrations of 0.10 ppm (frequently the lowest concentration used in the studies) for a few hours per day for several days to several weeks generally caused significant yield reductions. Although it appears from this analysis that a higher O_3 concentration was required to cause an effect than was estimated from the regression studies, it should be noted that the concentrations derived from the regression studies were based on a 10 percent yield loss, while in studies using analysis of variance (Table 6-36) the 0.10 ppm concentration frequently induced mean yield losses of 10 to 50 percent.

6.8.3.3 Yield Loss: Determination with Chemical Protectants. Chemical protectants (antioxidants) have been used to estimate the impact of ambient O_3 on crop yield. In these studies, some plots were treated with the chemical and others were not. Yield loss was determined by comparing the yield in the plots treated with the chemical to the yield in untreated plots. When chemical protectants are used, care must be used in interpreting the data because the chemical itself may alter plant growth. The chemical may not be effective

TABLE 6-36. OZONE CONCENTRATIONS AT WHICH SIGNIFICANT YIELD LOSSES HAVE BEEN NOTED FOR A VARIETY OF PLANT SPECIES EXPOSED UNDER VARIOUS EXPERIMENTAL CONDITIONS

Plant species	Exposure duration	Yield reduction, % of control	O_3 concentration, ppm	Reference
Alfalfa	7 hr/day, 70 days	51, top dry wt	0.10	Neely et al. (1977)
Alfalfa	2 hr/day, 21 day	16, top dry wt	0.10	Hoffman et al. (1975)
Pasture grass	4 hr/day, 5 days/wk, 5 wk	20, top dry wt	0.09	Horsman et al. (1980)
Ladino clover	6 hr/day, 5 days	20, shoot dry wt	0.10	Blum et al. (1982)
Soybean	6 hr/day, 133 days	55, seed wt/plant	0.10	Heagle et al. (1974)
Sweet corn	6 hr/day, 64 days	45, seed wt/plant	0.10	Heagle et al. (1972)
Sweet corn	3 hr/day, 3 days/wk, 8 wk	13, ear fresh wt	0.20	Oshima (1973)
Wheat	4 hr/day, 7 day	30, seed yield	0.20	Shannon and Mulchi (1974)
Radish	3 hr	33, root dry wt	0.25	Adedipe and Ormrod (1974)
Beet	2 hr/day, 38 days	40, storage root dry wt	0.20	Ogata and Maas (1973)
Potato	3 hr/day, every 2 wk, 120 days	25, tuber wt	0.20	Pell et al. (1980)
Pepper	3 hr/day, 3 days/wk, 11 wk	19, fruit dry wt	0.12	Bennett et al. (1979)
Cotton	6 hr/day, 2 days/wk, 13 wk	62, fiber dry wt	0.25	Oshima et al. (1979)
Carnation	24 hr/day, 12 days	74, no. of flower buds	0.05-0.09	Feder and Campbell (1968)
Coleus	2 hr	20, flower no.	0.20	Adedipe et al. (1972)
Begonia	4 hr/day, once every 6 days for a total of 4 times	55, flower wt	0.25	Reinert and Nelson (1979)
Ponderosa pine	6 hr/day, 126 days	21, stem dry wt	0.10	Wilhour and Neely (1977)
Western white pine	6 hr/days, 126 days	9, stem dry wt	0.10	Wilhour and Neely (1977)
Loblolly pine	6 hr/day, 28 days	18, height growth	0.05	Wilhour and Neely (1977)
Pitch pine	6 hr/day, 28 days	13, height growth	0.10	Wilhour and Neely (1977)
Poplar	12 hr/day, 5 mo	+1333, leaf abscission	0.041	Wilhour and Neely (1977)
Hybrid poplar	12 hr/day, 102 days	58, height growth	0.15	Patton (1981)
Hybrid poplar	8 hr/day, 5 day/wk, 6 wk	50, shoot dry wt	0.15	Patton (1981)
Red maple	8 hr/day, 6 wk	37, height growth	0.25	Dochinger and Townsend (1979)
American sycamore	6 hr/day, 28 days	9, height growth	0.05	Kress and Skelly (1982)
Sweetgum	6 hr/day, 28 days	29, height growth	0.10	Kress and Skelly (1982)
White ash	6 hr/day, 28 days	17, total dry wt	0.15	Kress and Skelly (1982)
Green ash	6 hr/day, 28 days	24, height growth	0.10	Kress and Skelly (1982)
Willow oak	6 hr/day, 28 days	19, height growth	0.15	Kress and Skelly (1982)
Sugar maple	6 hr/day, 28 days	12, height growth	0.15	Kress and Skelly (1982)

against all concentrations of all pollutants in the study area, which would result in an underestimation of yield loss. With an understanding of these limitations, however, researchers have concluded that chemical protectants are an objective method of assessing the effects of O_3 on crop yield, especially in conjunction with other methods. Results of several studies with chemical protectants showed decreased crop yield from exposure to ambient oxidants (Table 6-37). Crop yields were reduced 18 to 41 perecent when the ambient oxidant concentration exceeded 0.08 ppm for 5 to 18 days over the growing season of the crop.

6.8.3.4 Yield Loss: Determination from Ambient Exposures. A number of research studies have demonstrated that ambient O_3 concentrations in a number of locations in the United States are sufficently high to impair plant yield. Of studies to determine the impact of ambient oxidants (primarily O_3) on plant yield, most have compared the yield differences between plants grown in ambient air and those grown in charcoal-filtered air. Early research documented that ambient oxidants reduced the yield and quality of citrus, grape, tobacco, cotton, and potato (U.S. Environmental Protection Agency, 1978). Subsequent studies substantiated the impacts of ambient oxidants on plant yield (Table 6-38). Over several years, bean yields varied from a 5 percent increase to a 22 percent decrease in response to O_3 concentrations in excess of 0.06 ppm (Heggestad and Bennett, 1981).

Studies conducted on eastern white pine in the southern Appalachian mountains showed that ambient O_3 may have reduced the radial growth of sensitive individuals as much as 30 to 50 percent annually over the last 15 to 20 years (Mann et al., 1980). Field studies in the San Bernardino National Forest showed that during the last 30 years ambient O_3 may have reduced height growth of ponderosa pine by as much as 25 percent, radial growth by 37 percent, and the total wood volume produced by 84 percent (Miller et al., 1982). Calculations of biomass in these studies were based, however, on apparent reductions in radial growth without standardization of radial growth data with respect to tree age.

6.8.3.5 Yield Loss Summary. Several general conclusions can be drawn from the various approaches used to estimate crop yield loss. The data from the comparisons of crop yield in charcoal-filtered and unfiltered air (ambient exposures) clearly show that ambient levels of O_3 are sufficiently elevated in several parts of the country to impair the growth and yield of plants. The data from the chemical protectant studies support and extend this conclusion

TABLE 6-37. EFFECTS OF OZONE ON CROP YIELD AS DETERMINED BY THE USE OF CHEMICAL PROTECTANTS[a]

Species	Yield reduction,[b] % of control	O_3 exposure, ppm	Reference
Beans (green)	41	>0.08 for total of 27 hr over 3.5 months	Manning et al. (1974)
Onion	38	>0.08 on 5 days out of 48	Wukasch and Hofstra (1977b)
Tomato	30	>0.08 on 15 days over 3 months	Legassicke and Ormrod (1981)
Bean (dry)	24	>0.08 on 11 days (total of 34 hr) over 3 months	Temple and Bisessar (1979)
Tobacco	18	>0.08 on 14 days during the summer	Bisessar and Palmer (1984)
Potato	36	>0.08 ppm on 18 days (total of 68 hr) over 3 months	Bisessar (1982)
Potato	25	-[c]	Clarke et al. (1983)

[a] All the species were treated with the antioxidant, EDU, except the bean study by Manning et al. (1974) which used the systemic fungicide, benomyl.

[b] Yield reduction was determined by comparing the yields of plants treated with chemical protectants (control) to those that were not treated.

[c] This study was run over 2 years when the O_3 doses were 65 and 110 ppm-hr, respectively, but the yield loss was similar both years.

TABLE 6-38. EFFECTS OF AMBIENT OXIDANTS ON YIELD OF SELECTED CROPS

Plant species	O_3 concentration, ppm	Exposure duration	Yield, % reduction from control	Location of study	Reference
Tomato (Fireball 861 VR)	0.035 (0.017-0.072)	99 day average (6:00 a.m. - 9:00 p.m.)	33, fruit fresh wt	New York	MacLean and Schneider (1976)
Bean (Tendergreen)	0.041 (0.017-0.090)	43 day average (6:00 a.m. - 9:00 p.m.)	26, pod fresh wt		
Snap bean (3 cultivars: Astro, BBL 274, BBL 290)	0.042	3 mo average (9:00 a.m. - 8:00 p.m.)	1, pod wt	Maryland	Heggestad and Bennett (1981)
Soybean (4 cultivars: Cutler, York, Clark, Dare)	>0.05	31% of hr between 8:00 a.m. - 10:00 p.m. from late June to mid-September over three summers; 5% of the time the concentration was >0.08 ppm	20, seed wt	Maryland	Howell et al. (1979); Howell and Rose (1980)
Forbs, grasses, sedges	0.052	1979, 8 hr/day average (10:00 a.m. - 6:00 p.m.), April-September	32, total above-ground biomas	Virginia	Duchelle et al. (1983)
	0.051	1980, 8 hr/day average (10:00 a.m. - 6:00 p.m.), April-September	20, total above-ground biomass	Virginia	
	0.035	1981, 8 hr/day average (10:00 a.m. - 6:00 p.m.), April-September	21, total above-ground biomass		
Sweet corn (Bonanza)	>0.08	58% of hr (6:00 a.m. 9:00 p.m.), 1 July-6 September	9, ear fresh wt	California	Thompson et al. (1976a)
(Monarch Advance)	>0.08		28, ear fresh wt		

to other plant species. Both approaches indicate that the effects occur at low mean concentrations, with only a few O_3 occurrences greater than 0.08 ppm. Growth and yield data from the previous criteria document (U.S. Environmental Protection Agency, 1978), shown in Figure 6-25, indicate that effects on growth and yield of several plant species occurred when the mean O_3 concentration (for 4 to 6 hr/day) exceeded 0.05 ppm for at least 2 wk. The data from the regression studies, conducted to develop exposure-response functions for estimating yield loss, indicated that at least 50 percent of the species/cultivars tested were predicted to display a 10 percent yield loss at 7-hr seasonal mean O_3 concentrations of 0.05 ppm or less. Most of the data from the discrete treatment studies did not use levels low enough to support these values directly. The magnitude of yield losses reported at 0.10 ppm, however, indicate that maintenance of a substantially lower concentration than 0.10 ppm is needed to prevent O_3 effects, although a specific value cannot be derived from the discrete treatment studies.

6.8.4 Effects on Crop Quality

Based on results of the few studies that have been conducted, O_3 can reduce crop quality in addition to reducing the total yield of the crop. Quality is a general term that includes many features of the crop, such as nutritional composition, appearance, taste, and ability to withstand storage and shipment. Examples of O_3-induced alterations in quality are decreased oil in soybean seeds (Howell and Rose, 1980; Kress and Miller, 1983); decreased β-carotene, vitamin C, and carbohydrates in alfalfa (Thompson et al., 1976b; Neely et al., 1977); and increased reducing sugars that are associated with undesirable darkening when potatoes are used to make potato chips (Pell et al., 1980).

6.8.5 Statistics Used to Characterize Ozone Exposures

The characterization and representation of plant exposures to O_3 has been, and continues to be a major problem. Research has not yet clearly identified which components of the pollutant exposure cause the plant response. Most studies have characterized the exposure by the use of mean O_3 concentrations, although various averaging times have been used. Some studies have also used cumulative O_3 dose. The difficulty of selecting an appropriate statistic to characterize plant exposure has been summarized by Heagle and Heck (1980). Ambient and experimental O_3 exposures have been presented as seasonal, monthly, weekly, or daily means; peak hourly means; number of hours above a selected concentration; or the number of hours above selected concentration intervals. None of these statistics adequately characterize the relationships among O_3 concentration, exposure duration, interval between exposures, and plant response. The use of a mean concentration (with long averaging times) (1) implies that all concentrations of O_3 are equally effective in causing plant responses and (2) minimizes the contributions of the peak concentrations to the resonse. The mean treats low-level, long-term exposures the same as high-concentration, short-term ones. Thus, the use of a long-term mean concentration ignores the importance of peak concentrations; to ignore the peaks is inconsistent with the literature.

The total ozone dose (concentration multiplied by time) has been used to describe plant exposure; however, it suffers from the same problem as the mean. The total dose is simply the summation of the ppm-hr over the study period, which also treats all concentrations as being equally effective. Several investigators have attempted to give greater importance to peak O_3 concentrations. For example, Oshima et al. (1977a,b) and Lefohn and Benedict (1982) have summed only the ppm-hr of exposure greater than some preselected value. Larsen et al. (1983) have introduced the concept of "impact" to describe the effects of O_3 and SO_2 on soybeans. The "impact (I)" is calculated similarly to total dose, except the concentration is raised to an exponent greater than one ($I = C^W \times T$); this method of calculation effectively gives greater weight to the higher concentrations. More recently, Larsen and Heck (1984) have suggested the term "effective mean" to describe an approach in which greater importance is given to higher concentrations. The "effective mean" is defined as the average hourly impact raised to an exponent and divided by the duration.

Several lines of evidence suggest that higher concentrations should be regarded as having the greater influence in determining the impact of O_3 on vegetation. Studies have shown that plants can tolerate some combinations of exposure duration and concentration without exhibiting foliar injury or effects on growth or yield, illustrating that not all concentrations are equally effective in causing a response. From the toxicological perspective, it is the peaks or concentrations above some level that are most likely to have an impact. Effects occur on vegetation when the amount of pollutant that the plant has absorbed exceeds the ability of the organism to repair or compensate for the impact.

Studies with beans and tobacco (Heck et al., 1966) showed that a dose (concentration times time) distributed over a short period induced more injury than did the same dose distributed over a longer period. Tobacco studies showed that the O_3 concentration was substantially more important than exposure duration in causing foliar injury (Tonneijck, 1984). In beans, foliar injury occurred when the internal O_3 flux exceeded 115 μmoles/m^2 in 1 hr (Bennett, 1979). A single 3-hr exposure, however, at approximately half the concentration (0.27 compared with 0.49 ppm) required a 64 percent greater internal flux of O_3 to produce the same amount of foliar injury as the 1-hr exposure required. More recently, Amiro et al. (1984) showed that higher concentrations were more important than low concentrations in causing injury. Their study also suggested the existence of a biochemical injury threshold (i.e., the O_3 uptake rates that plants can experience without incurring visible foliar injury). The greater importance of concentration compared to exposure duration has also been reported by other authors (e.g., Heck and Tingey, 1971; Henderson and Reinert, 1979; Reinert and Nelson, 1979).

Studies with soybean (Johnston and Heagle, 1982), tobacco (Heagle and Heck, 1974), and bean (Runeckles and Rosen, 1977) showed that plants exposed to a low level of O_3 for a few days became more sensitive to subsequent O_3 exposures. In studies with tobacco, Mukammal (1965) showed that a high O_3 concentration on one day caused substantial injury, whereas an equal or higher concentration on the second day caused only slight injury. Using stress ethylene as an indicator of O_3 effects, Stan and Schicker (1982) showed that a series of successive short exposures was more injurious to plants than a continuous exposure at the same O_3 concentration for the same total exposure period. Walmsley et al. (1980) continuously exposed radishes to O_3 for several weeks and found that the plants acquired some O_3 tolerance. The acquired tolerance displayed two components: (1) the exposed plants developed new leaves faster than the controls, and (2) there was a progressive decrease in sensitivity of the new leaves to O_3. The newer leaves also displayed a slower rate of senescence. The observations by Elkiey and Ormrod (1981) that the O_3 uptake decreased during a 3-day study period may provide an explanation for the results with radish.

Not only are concentration and time important but the dynamic nature of the O_3 exposure is also important; i.e. whether the exposure is at a constant or variable concentration. Musselman et al. (1983) recently showed that constant concentrations of O_3 caused the same types of plant responses as variable concentrations at equivalent doses. Constant concentrations, however, had less effect on plant growth responses than variable concentrations at similar doses. Exposures of radishes to ambient O_3 in open-top exposure chambers showed that significant yield reductions occurred when the maximum O_3 concentration exceeded 0.06 ppm at least 10 percent of the days when the crop was growing (Ashmore, 1984). Initial studies have compared the response of alfalfa to daily peak and episodic O_3 exposure profiles that gave the equivalent total O_3 dose over the growing season (Hogsett et al., 1985). Alfalfa yield was reduced to a greater extent in the episodic than in the daily peak exposure. This study also illustrates the problem with the 7-hr seasonal mean concentration; i.e., it does not properly account for the peak concentrations. The plants that displayed the greater growth reduction (in the episodic exposure) were exposed to a significantly lower 7-hr seasonal mean concentration. Studies with SO_2 also showed that plants exposed to variable concentrations exhibited a greater plant response than those exposed to a constant concentration (McLaughlin et al., 1979; Male et al., 1983).

6.8.6 Relationship Between Yield Loss and Foliar Injury

Because plant growth and production depend on photosynthetically functional leaves, various studies have been conducted to determine the association between foliar injury and yield for species in which the foliage is not part of the yield. Some research has demonstrated significant yield loss with little or no foliar injury (e.g., Tingey et al., 1971a; Tingey and Reinert, 1975; Kress and Skelly, 1982; Feder and Campbell, 1968; Adedipe et al., 1972). Other studies showed that significant foliar injury was not always associated with yield loss (Heagle et al., 1974; Oshima et al., 1975). The relative sensitivities of two potato cultivars were reversed when judged by foliar injury versus yield reductions (Pell et al., 1980). In field corn, foliar injury occurred at a lower O_3 concentration than yield reductions; but as the O_3 concentration increased, yield was reduced to a greater extent than foliar injury was increased (Heagle et al., 1979a). In wheat, foliar injury was not a good predictor of O_3-induced yield reductions (Heagle et al., 1979b).

6.8.7 Physiological Basis of Yield Reductions

As discussed earlier in this summary, plant growth is the summation of a series of biochemical and physiological processes related to uptake, assimilation, biosynthesis, and translocation. An impairment in these processes may lead to reduced plant yield if the process is limiting.

For plant growth to occur, plants must assimilate CO_2 and convert it into organic substances; an inhibition in carbon assimilation may be reflected in plant growth or yield. In several species O_3 (at 0.05 ppm and higher) inhibited photosynthesis, as measured by gas-exchange (e.g., U.S. Environmental Protection Agency, 1978; Coyne and Bingham, 1978; Black et al., 1982; Bennett and Hill, 1974; Yang et al., 1983). Biochemical studies showed that O_3 (0.12 ppm for 2 hr) inhibited an enzyme that catalyzes the assimilation of CO_2 (Pell and Pearson, 1983).

Ozone, in addition to decreasing the total amount of CO_2 that is assimilated, alters that pattern by which the reduced amount of assimilate is partitioned throughout the plant. There is generally less photosynthate translocated to the roots and to the reproductive organs (e.g., Tingey et al., 1971a; Jacobson, 1982; Oshima et al., 1978, 1979; Bennett et al., 1979). This reduces root size and marketable yield as well as rendering the plant more sensitive to injury from environmental stresses. Another consequence of reduced root growth and altered carbon allocation is an impairment of symbiotic nitrogen fixation (U.S. Environmental Protection Agency, 1978; Ensing and Hofstra, 1982).

The reproductive capacity (flowering and seed set) is reduced by O_3 in ornamental plants, soybean, corn, wheat, and other plants (Adedipe et al., 1972; Feder and Campbell, 1968; Heagle et al., 1972, 1974; Shannon and Mulchi, 1974). These data suggest that O_3 impairs the fertilization process in plants. This suggestion has been confirmed in tobacco and corn studies using low concentrations of O_3 (0.05 to 0.10 ppm) for a few hours (Feder, 1968; Mumford et al., 1972).

Ozone both in the field and in chamber studies stimulates premature senescence and leaf drop (Menser and Street, 1962; Heagle et al., 1974; Heggestad, 1973; Pell et al., 1980; Hofstra et al., 1978). In part, the O_3-induced yield reduction has been attributed to premature senescence. The premature leaf drop decreases the amount of photosynthate that a leaf can contribute to plant growth.

6.8.8 Factors Affecting Plant Response to Ozone

Numerous factors influence the type and magnitude of plant response to O_3. Most studies of the factors influencing plant response have been limited to effects on foliar injury; however, some studies have measured yield and some have researched the physiological basis for the influences. The parameters studied include environmental factors, biological factors, and interactions with other air pollutants.

6.8.8.1 Environmental Conditions. Environmental conditions before and during plant exposure are more influential than post-exposure conditions in determining the magnitude of the plant response. The influence of environmental factors has been studied primarily under controlled conditions, but field observations have substantiated the results. Most studies have evaluated the influence of only a single environmental factor and have relied primarily upon foliar injury as the plant response measure. Some generalizations of the influence of environmental factors can be made:

1. Light conditions that are conducive to stomatal opening appear to enhance O_3 injury (U.S. Environmental Protection Agency, 1978). Light is required to induce stomatal opening, which permits the plant to absorb pollutants.
2. No consistent pattern relating plant response to temperature has been observed (U.S. Environmental Protection Agency, 1978). Plants do not appear to be as sensitive at extremely high or low temperatures, however, as they are under more moderate conditions.
3. Plant injury tends to increase with increasing relative humidity (U.S. Environmental Protection Agency, 1978). The relative humidity effect appears to be related to stomatal aperture, which tends to increase with increasing relative humidity. McLaughlin and Taylor (1981) demonstrated that plants absorb significantly more O_3 at high humidity than at low humidity. It is generally accepted that plants in the eastern United States are injured by lower concentrations of O_3 than their counterparts in California; this phenomenon has been attributed to differences in humidity (U.S. Environmental Protection Agency, 1978).
4. As soil moisture decreases, plant water stress increases and there is a reduction in plant sensitivity to O_3 (U.S. Environmental Protection Agency, 1978). The reduced O_3 sensitivity is apparently related to stomatal closure, which reduces O_3 uptake (U.S. Environmental Protection Agency, 1978; Olszyk and Tibbitts, 1981; Tingey et al., 1982). Water stress does not confer a permanent tolerance to O_3;

once the water stress has been alleviated, the plants regain their sensitivity to O_3 (Tingey et al., 1982).

6.8.8.2 *Interaction with Plant Diseases*. Ozone can affect the development of disease in plant populations. Laboratory evidence suggests that O_3 (at ambient concentrations or greater for 4 hr or more) inhibits infection by pathogens and subsequent disease development (Laurence, 1981; Heagle, 1982; U.S. Environmental Protection Agency, 1978). Increases, however, in diseases from "stress pathogens" have been noted. For example, plants exposed to O_3 were more readily injured by *Botrytis* than plants not exposed to O_3 (Manning et al., 1970a,b; Wukasch and Hofstra, 1977a,b; Bisessar, 1982). Both field and laboratory studies have confirmed that the roots and cut stumps of O_3-injured ponderosa and Jeffrey pines are more readily colonized by a root rot (*Heterobasidion annosus*). The degree of infection was correlated with the foliar injury (James et al., 1980a; Miller et al., 1982). Studies in the San Bernardino National Forest showed that O_3-injured trees were predisposed to attack by bark beetles and that fewer bark beetles were required to kill an O_3-injured tree (Miller et al., 1982).

6.8.8.3 *Interaction of Ozone with Other Air Pollutants*. The report of Menser and Heggestad (1966) provided the initial impetus for studying the interaction of O_3 with SO_2. They showed that Bel W-3 tobacco plants exposed to O_3 (0.03 ppm) or SO_2 (0.24 to 0.28 ppm) were uninjured but that substantial foliar injury resulted when the plants were exposed to both gases simultaneously. Subsequent studies have confirmed and extended the observation that combinations of O_3 and SO_2 may cause more visible injury than expected based on the injury from the individual gases. This injury enhancement (synergism) is most common at low concentrations of each gas and also when the amount of foliar injury induced by each gas, individually, is small. At higher concentrations or when extensive injury occurs, the effects of the individual gases tend to be less than additive (antagonistic). In addition to foliar injury, the effects of pollutant combinations have also been investigated in relation to other plant effects, and these have been discussed in several reviews and numerous individual reports (e.g., Reinert et al., 1975; Ormrod, 1982; Jacobson and Colavito, 1976; Heagle and Johnston, 1979; Olszyk and Tibbitts, 1981; Flagler and Youngner, 1982a; Foster et al., 1983b; Heggestad and Bennett, 1981; Heagle et al., 1983a).

Field studies have investigated the influence of SO_2 on plant response to O_3 at ambient and higher concentrations in several plant species: soybean (Heagle et al., 1983c; Reich and Amundson, 1984), beans (Oshima, 1978; Heggestad and Bennett, 1981), and potatoes (Foster et al., 1983b). In these studies, O_3 altered plant yield but SO_2 had no significant effect and did not interact with O_3 to reduce plant yield unless the SO_2 exposure concentrations and frequency of occurrence were much greater than the concentrations and frequencies of occurrence typically found in the ambient air in the United States.

The applicability of the yield results from pollutant combination studies to ambient conditions is not known. An analysis of ambient air monitoring data for instances of co-occurrence of O_3 and SO_2 indicated that at sites where the two pollutants were monitored, they both were present for ten or fewer periods during the growing season (Lefohn and Tingey, 1984). Co-occurrence was defined as the simultaneous occurrence of hourly averaged concentrations of 0.05 ppm or greater for both pollutants. At this time, it appears that most of the studies of the effects on pollutant combinations (O_3 and SO_2) on plant yield have used a longer exposure duration and a higher frequency of pollutant co-occurrence than are found in the ambient air.

Only a few studies have investigated the effects of O_3 when combined with pollutants other than SO_2, and no clear trend is available. Preliminary studies using three-pollutant mixtures (O_3, SO_2, NO_2) showed that the additions of SO_2 and NO_2 (at low concentrations) caused a greater growth reduction than O_3 alone.

6.8.9 Economic Assessment of Effects of Ozone on Agriculture

Evidence from the plant science literature clearly demonstrates that O_3 at ambient levels will reduce yields of some crops (see Section 6.4.3.2.2). In view of the importance of U.S. agriculture to both domestic and world consumption of food and fiber, such reductions in crop yields could adversely affect human welfare. The plausibility of this premise has resulted in numerous attempts to assess, in monetary terms, the losses from ambient O_3 or the benefits of O_3 control to agriculture. Many of these assessments have been performed since publication of the 1978 O_3 criteria document (U.S. Environmental Protection Agency, 1978). The utility of these post-1978 studies in regulatory decision-making can be evaluated in terms of how well the requisite biological, aerometric, and economic inputs conform to specific criteria, as discussed in Section 6.5.

While a complete discussion of the criteria for evaluating economic assessments is not appropriate here, it is instructive to highlight certain key issues. First, the evidence on crop response to O_3 should reflect how crop yields will respond under actual field conditions. Second, the air quality data used to frame current or hypothetical effects of O_3 on crops should represent the actual exposures sustained by crops in each production area. Finally, the assessment methodology into which such data are entered should (1) capture the economic behavior of producers and consumers as they adjust to changes in crop yields and prices that may accompany changes in O_3 air quality; and (2) ideally, should accurately reflect institutional considerations, such as regulatory programs, that may result in market distortions.

The assessments of O_3 damages to agriculture found in the literature display a range of procedures for calculating economic losses, from simple monetary calculation procedures to more complex economic assessment methodologies. The simple procedures calculate monetary effects by multiplying predicted yield or production changes resulting from exposure to O_3 by an assumed constant crop price, thus failing to recognize possible crop price changes arising from yield changes as well as not accounting for the processes underlying economic response. Conversely, a rigorous economic assessment will provide estimates of the benefits of air pollution control that account for producer-consumer decision-making processes, associated market adjustments, and perhaps some measure of distributional consequences between affected parties. It is important to distinugish between those studies based on naive or simple models and those based on correct procedures, since the naive procedure may be badly biased, leading to potentially incorrect policy decisions.

Most of the post-1978 economic assessments focus on O_3 effects in specific regions, primarily California and the Corn Belt (Illinois, Indiana, Iowa, Ohio, and Missouri). This regional emphasis may be attributed to the relative abundance of data on crop response and air quality for selected regions, as well as the national importance of these agricultural regions. Economic estimates for selected regions are presented in Table 6-39. In addition to reporting the monetary loss or benefit estimates derived from each assessment, this table provides some evaluation of the adequacy of the plant science, aerometric, and economic data, and assumptions used in each assessment. Adequacy as defined here does not mean that the estimates are free of error; rather, it implies that the estimates are based on the most defensible biologic,

TABLE 6-39. SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Reference and study region	Crops	Annual benefits of control, $ million	Evaluation of critical data and assumptions[a]			Additional comments
			Plant response data	Aerometric data	Economic model data	
Adams et al. (1982); Southern California	12 annual crops: beans, broccoli, cantaloupes, carrots, cauliflower, celery, lettuce, onions, potatoes, tomatoes cotton, and sugar beets.	$45 (in 1976 dollars)	Inadequate; uses Larsen-Heck (1976) foliar injury models converted to yield losses.	Adequate; exposure measured as cumulative seasonal exposure in excess of California standard (0.08 ppm), from hourly data collected for sites closest to production regions.	Adequate; a price endogenous mathematical (quadratic) programming model reflecting agronomic, environmental, and economic conditions in 1976.	Economic effect measured as a change in economic surplus (sum of consumers and producers' surpluses) between base case (actual O_3 levels in 1976) and economic surplus that would be realized if all regions were in compliance with 1971 photochemical oxidant standard of 0.08 ppm.
Lueng et al. (1982); Southern California	9 crops: lemons, oranges (Valencia and Navel), strawberry, tomato, alfalfa, avocado, lettuce, and celery.	$103 (in 1975 dollars)	Inadequate; O_3-yield response functions estimated from secondary data on crop yields.	Adequate for some regions; exposure measured in average monthly concentration in ppm for 12 hr period (7:00 a.m. to 7:00 p.m.). Data from 61 Calfornia Air Resources Board monitoring sites.	Adequate on demand side; economic model is composed of linear supply and demand curves for each crop estimated with data from 1958-1977, but ignores producer-level adjustments.	Economic effect is measured as a change in economic surplus between base case (1975) and a clean air environment reflecting zero O_3.
Howitt et al. (1984a,b); California	13 crops: alfalfa, barley, beans, celery, corn, cotton, grain sorghum, lettuce, onions, potatoes, rice, tomatoes, and wheat.	From $35 (benefit of control to 0.04 ppm) to $157 (loss for increase to 0.08 ppm) (in 1978 dollars).	Adequate for some crops; most response functions derived from NCLAN data through 1982. Surrogate responses used for celery, onions, rice and potatoes are questionable.	Adequate; California Air Resources Board data for monitoring sites closest to rural production areas. Exposure measured as the seasonal 7-hr average in each production area for compatibility with NCLAN exposure.	Adequate; economic model similar to Adams et al. (1982) but includes some perennial crops and reflects 1978 economic and technical environment.	Economic effects measured as changes in economic surplus across three O_3 changes from 1978 actual levels. These include changes in ambient O_3 to 0.04, 0.05, and 0.08 ppm across all regions.

TABLE 6-39 (cont'd). SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Reference and study region	Crops	Annual benefits of control, $ million	Evaluation of critical data and assumptions[a]			Additional comments
			Plant response data	Aerometric data	Economic model data	
Rowe et al. (1984); San Joaquin Valley in California	14 annual and perennial crops: alfalfa, barley, beans, carrots, corn, cotton, grain sorghum, grass hay, grapes, pasture, potatoes, safflower, tomatoes and wheat.	$43 to $117 depending on degree of control, measured in 1978 dollars.	Adequate for some crops; response functions based on both experimental and secondary data. Most crops from NCLAN data. Responses for the remaining crops were based on surrogate responses of similar crops in the data set.	Adequate; 4 exposure levels were tested. The average hourly concentration was used in most functions to predict changes. All data were from California Air Resources Board monitoring sites in predominantly rural areas.	Adequate; same as in Howitt et al. (1984a,b).	Economic effects measured as the change in economic surplus between the 1978 base case and three increasingly stringent control scenarios: (1) a 50% reduction in in no. of hr $\geq$0.10 ppm; (2) meeting the current standard of 0.10 ppm; and (3) meeting an O_3 standard of 0.08 ppm.
Adams and McCarl (1985); Corn Belt	3 crops: corn, soybeans, and wheat.	$668 (in 1980 dollars)	Adequate; O_3 yield response information from NCLAN for 3 yr (1980-1982). Yield adjustments estimated from Weibull response models.	Adequate except for linkage of 7-hr seasonal mean to hourly standards. Data are interpolated from SAROAD monitoring sites by Kriging[b] procedure, measured as 1980 seasonal 7-hr average. Regulatory analysis assumes that O_3 is log-normally distributed.	Adequate; economic estimates are generated by a mathematical programming model of U.S. agriculture reflecting 1980 conditions. Farm-level response is portrayed by 12 individual "representative" farm models to generate supply adjustments used in the national-level model.	Economic estimates represent changes in economic surplus (sum of consumers' and producers' surpluses) between current (1980) O_3 levels and increases and decreases in ambient O_3 levels. Reduction to a uniform ambient level of 0.04 ppm across all regions results in benefits of $668 million.

TABLE 6-39 (cont'd). SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Reference and study region	Crops	Annual benefits of control, $ million	Evaluation of critical data and assumptions[a]			Additional comments
			Plant response data	Aerometric data	Economic model data	
Mjelde et al. (1984); Illinois	3 crops: corn, soybeans, and wheat.	Ranges from \$55 to \$220 annually for period 1976 to 1980.	Adequate when cross-checked against NCLAN data; responses are estimated from secondary (non-experimental) data on actual farmer yield, input, and O_3 concentrations. Results are translated into yield effects and compared to NCLAN data from Illinois.	Adequate; same Kriged data set as used in Adams and McCarl (1985), except only for Illinois and cover 5 yr (1976-1980). Exposure is measured as seasonal 7-hr average to facilitate comparison with NCLAN response estimates.	Adequate at producers level; economic model consists of a series of annual relationships on farmers' profits These functions). These functions are adjusted to represent changes in O_3 (±25%) for each year. Model does not include consumer (demand) effects.	The estimates represent increases in farmers' profits that could arise for a 25% reduction in O_3 for each year (1976-1980). Years with higher ambient levels have highest potential increase in profits for changes.
Page et al. (1982); Ohio River Basin	3 crops: corn, soybeans and wheat.	\$7.022 measured as present value of producer losses for period 1976 to 2000. Annualized losses are approx. \$270 in 1976 dollars.	Inadequate; crop losses provided by Loucks and Armentano (1982); responses derived by synthesis of existing experimental data.	Inadequate; dose measured as cumulative seasonal exposure for a 7-hr period (9:30 a.m. to 4:30 p.m.) Monitoring sites at only 4 locations were used to characterize the regional exposure.	Inadequate; the economic model consists of regional supply curves for each crop. The predicted changes in production between "clean air" case and each scenario are used to shift crop supply curves. The analysis ignores price changes from shifts in supply.	Losses are measured as differences in producer surplus across the various scenarios. Since prices are assumed fixed (in real terms) over the period, no consumer effects are measured.

TABLE 6-39 (cont'd). SUMMARY OF ESTIMATES OF REGIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Reference and study region	Crops	Annual benefits of control, $ million	Evaluation of critical data and assumptions[a]			Additional comments
			Plant response data	Aerometric data	Economic model data	
Benson et al. (1982); Minnesota	4 crops: alfalfa, wheat, corn, and potatoes. Cultivar believed to be limited to one per crop.	$30.5 (measured in 1980 dollars)	Inadequate; but innovative crop loss models estimated using experimental yield-O_3 data from other researchers. Crop loss modeling includes both chronic and espisodic response and crop development stage as factors in yield response, by regressing yield on O_3 exposures for various time windows, during the growing season.	Adequate, air quality data are for state of Minnesota for 1979 and 1980. Exposure measured several ways but generally as a daily exposure statistic reflecting either sum of hourly averages or the mean hourly average.	Adequate on demand side; The economic estimates are derived from a comprehensive economic model calibrated to 1980 values.	The economic effect measured in terms of short-run profit changes for Minnesota producers. If yields are assumed to change only in Minnesota then losses to Minnesota producers are $30.5 million. If yields change in Minnesota and the rest of U.S., then producers gain $67 million as a result of increases in crop prices.

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[a] Adequacy as defined here does not mean that the estimates are free of error; rather, it implies that the estimates are based on the most defensible biologic, aerometric, or economic information and models currently available.

[b] Kriging is a spatial interpolation procedure that has been used to generate O_3 concentration data for rural areas in which no monitoring sites have been established. See Heck et al. (1983b).

aerometric, or economic information and models currently available in the literature. The estimates can then be ranked relative to the strength of these data and assumptions. Of the eight regional studies reviewed, most have adequate economic models, but only four are judged adequate across all input categories. Further, most regional studies abstract from the interdependencies that exist between regions, which limits their utility in evaluating secondary national ambient air quality standards (SNAAQS).

National-level studies can overcome this limitation of regional analyses by accounting for economic linkages between groups and regions. A proper accounting for these linkages, however, requires additional data and more complex models, and frequently poses more difficult analytical problems. Thus, detailed national assessments tend to be more costly to perform. As a result, there are fewer assessments of pollution effects at the national than at the regional level. Six national-level assessments performed since the last criteria document was published in 1978 are reported in Table 6-40. Of these, two used the simple "price times quantity" approach to quantify dollar effects. Four used more defensible economic approaches. As with Table 6-39, an evaluation of the adequacy of critical plant science, aerometric, and economic data is presented, along with the estimates of benefits or damages.

As is evident from the evaluation, most of the national studies reviewed here suffer from either plant science and aerometric data problems, incomplete economic models, or both. As a result of these limitations, decision-makers should be cautious in using these estimates to evaluate the efficiency of alternative SNAAQS. Two of the studies, however, are judged to be much more adequate in terms of the three critical areas of data inputs. Together, they provide reasonably comprehensive estimates of the economic consequences of changes in ambient air O_3 levels on agriculture.

In the first of these studies, Kopp et al. (1984) measured the national economic effects of changes in ambient air O_3 levels on the production of corn, soybeans, cotton, wheat, and peanuts. In addition to accounting for price effects on producers and consumers, the assessment methodology used is notable in that it placed emphasis on developing producer-level responses to O_3-induced yield changes (from NCLAN data) in 200 production regions. The results of the Kopp et al. (1984) study indicated that a reduction in O_3 from 1978 regional ambient levels to a seasonal 7-hr average of approximately 0.04 ppm would result in a $1.2 billion net benefit in 1978 dollars. Conversely,

TABLE 6-40. SUMMARY OF ESTIMATES OF NATIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study	Crops	Annual benefits of control, $ billion	Evaluation of critical data and assumptions[a]			Additional comments
			Plant response data	Aerometric data	Economic model data	
Ryan et al. (1981)	16 crops: alfalfa, beets, broccoli, cabbage, corn (sweet and field), hay, lima beans, oats, potatoes, sorghum, soybeans, spinach, tobacco, tomatoes, and wheat.	$1.747 (in 1980 dollars).	Inadequate; yield-response information derived from a synthesis of 5 yield studies in the literature prior to 1980. Synthesized response functions estimated for both chronic and acute exposures for six crops. For the remaining 10 crops surrogates are used. Yield changes are based on reductions in O_3 to meet 1980 Federal standard of 0.12 ppm in non-compliance counties.	Inadequate; dose measured in several ways to correspond to underlying response function. O_3 data derived from National Aerometric Data Bank and from Lawrence Berkeley Laboratory, for period 1974-1976.	Inadequate; naive economic model. Monetary impact calculated by multiplying changes in county production by crop price in 1980. Measures impact on producers only.	Dollar estimate is for the 531 counties exceeding the Federal standard of 0.12 ppm. This study is essentially an updated version of Benedict et al. (1971) reported in 1978 criteria document.
Shriner et al. (1982)	4 crops: corn, soybeans, wheat, and peanuts. Multiple cultivars of all crops but peanuts.	$3.0 (in 1978 dollars).	Adequate; analysis uses NCLAN response data for 1980. Functions estimated in linear form. Yield changes reflect difference between 1978 ambient O_3 levels of each county and assumed background of 0.025 ppm concentration.	Unknown; exposure may be measured as highest 7-hr. average, rather than 7-hr NCLAN average. Rural ambient concentrations for 1978 estimated by Kriging[b] procedure applied to SAROAD data.	Inadequate; same as Ryan et al. (1981) except uses 1978 crop prices.	Dollar estimates are for all counties producing the four crops. As with Ryan et al. (1981), estimates are for for producer level effects only.
Adams and Crocker (1984)	3 crops: corn, soybeans, and cotton. Two corn cultivars, three soybeans, two cotton.	$2.[illegible] (in 1980 dollars).	Adequate; analysis uses NCLAN O_3-yield data for 1980 and 1981. Functions estimated in linear form. Yield changes measured between 1980 ambient levels and an assumed O_3 concentration of 0.04 ppm across all production regions.	Adequate; 1980 ambient O_3 levels estimated by Kriging of SAROAD monitoring sites, translated into a seasonal 7-hr average.	Adequate on demand side; inadequate on modeling producer behavior; economic model consists of crop demand and supply curves. Corresponding price and quantity adjustments result in changes in economic surplus. No producer level responses modeled; only measures aggregate effects.	Economic estimate measured in terms of changes in consumer and producer surpluses associated with the change in O_3.

TABLE 6-40 (cont'd). SUMMARY OF ESTIMATES OF NATIONAL ECONOMIC CONSEQUENCES OF OZONE POLLUTION

Study	Crops	Annual benefits of control, $ billion	Evaluation of critical data and assumptions[a] Plant response data	Aerometric data	Economic model data	Additional comments
Adams et al. (1984a)	4 crops: corn, soybeans, wheat, and cotton. Two cultivars for corn and cotton, three for soybeans and and wheat.	$2.4 (in 1980 dollars).	Adequate; analysis uses NCLAN O_3-yield data for 1980 through 1982. Yield changes measured between 1980 ambient levels and 25% reduction in O_3 across all regions. Functions estimated in both linear and quadratic form.	Adequate; same as Adams and Crocker (1984).	Inadequate producer model; same as Adams and Crocker (1984), except that analysis examines range of economic estimates reflecting variability in yield predictions resulting from sample size and functional form.	Same as Adams and Crocker (1984). Linear functions result in higher yield losses and hence higher economic loss estimates. Reported estimate ($2.4 billion) is for quadratic response function.
Kopp et al. (1984)	5 crops: corn, soybeans, wheat, cotton, and peanuts. Multiple cultivars of each crop except peanuts.	$1.2 (in 1978 dollars).	Adequate; analysis uses NCLAN O_3 yield response data for 1980 through 1982. Yield losses (for estimates reported here) measured as the difference between ambient 1978 O_3 and a level assumed to represent compliance with an 0.08 ppm standard.	Adequate; same as Adams and Crocker (1984) and Adams et al. (1984b) but for 1978 growing season.	Adequate; economic model consists of producer-level models, by crop, for numerous production regions. Predicted yield changes are used to generate supply shifts for each region/crop combined with crop demand relationships to estimate producer and consumer surpluses.	In addition to measuring the change in economic surplus for various assumed O_3 levels, the analysis also includes an examination of the sensitivity of the estimates to the nature of the demand relationships used in the model.
Adams et al. (1984b)	6 crops: barley, corn, soybeans, cotton, wheat, and sorghum. Multiple cultivars used for each crop except barley and grain sorghum; two for cotton, three for wheat, two for corn, and nine for soybean.	$1.7 (in 1980 dollars).	Adequate; analysis uses NCLAN O_3 yield response data for 1980 through 1983. Yield changes reflect changes from 1980 ambient O_3 of 10 and 40% reduction and a 25% increase for each response.	Adequate; same as above but for 1980 and 1976 through 1980 periods.	Adequate; economic model consists of two components: a series of farm-level models for each of 55 production regions and a national model of crop use and demand. Yield changes are used to generate regional supply shifts used in national model.	Consumer surplus estimated for both domestic and foreign markets; producer surplus nationally and by region. The analysis includes a range of economic estimates reflecting changes in response and O_3 data and assumptions.

[a] Adequacy as defined here does not mean that the estimates are free of error; rather, it implies that the estimates are based on the most defensible biologic, aerometric, or economic information and models currently available.

[b] Kriging is a spatial interpolation procedure that has been used to generate O_3 concentration data for rural areas in which no monitoring sites have been established. See Heck et al. (1983b).

an increase in O_3 to an assumed ambient concentration of 0.08 ppm (seasonal 7-hr average) across all regions produced a net loss of approximately $3.0 billion.

The second study, by Adams et al. (1984b), is a component of the NCLAN program. The results were derived from an economic model of the U.S. agricultural sector that includes individual farm models for 55 production regions integrated with national supply-and-demand relationships for a range of crop and livestock activities. Using NCLAN data, the analysis examined yield changes for six major crops (corn, soybeans, wheat, cotton, grain, sorghum, and barley) that together account for over 75 percent of U.S. crop acreage. The estimated annual benefits (in 1980 dollars) from O_3 adjustments are substantial, but make up a relatively small percentage of total agricultural output (about 4 percent). Specifically, in this analysis, a 25 percent reduction in ozone from 1980 ambient levels resulted in benefits of $1.7 billion. A 25 percent increase in ozone resulted in an annual loss (negative benefit) of $2.363 billion. When adjusted for differences in years and crop coverages, these estimates are quite close to the Kopp et al. (1984) benefit estimates.

While the estimates from both Kopp et al. (1984) and Adams et al. (1984b) were derived from conceptually sound economic models and from the most defensible plant science and aerometric data currently available, there are several sources of uncertainty. These include the issue of exposure dynamics (7-hr per day exposures from the NCLAN experiments versus longer exposure periods, such as 12-hr exposures), and the lack of environmental interactions, particularly O_3-moisture stress interactions, in many of the response experiments. Also, the O_3 data in both studies are based on a limited set of the monitoring sites in the SAROAD system of EPA, mainly sites in urban and suburban areas. While the spatial interpolation process used for obtaining O_3 concentration data (Kriging) results in a fairly close correspondence between predicted and actual O_3 levels at selected validation points, validation requires more monitoring sites in rural areas. The economic models, with their large number of variables, and parameters, and the underlying data used to derive these values, contain potential sources of uncertainty, including the effects on benefits estimates of market-distorting factors such as the Federal farm programs.

The inclusion of these possible improvements in future assessments is not likely, however, with the possible exception of market-distorting factors, to alter greatly the range of agricultural benefits provided in the Kopp et al. (1984) and Adams et al. (1984b) studies, for several reasons. First, the current studies cover about 75 to 80 percent of U.S. agricultural crops (by value). For inclusion of the other 20 percent to change the estimates significantly would require that their sensitivities to O_3 be much greater than for the crops included to date. Second, model sensitivity analyses from existing studies indicate that changes in key plant science parameters must be substantial to translate into major changes in economic estimates. From experience to date it seems unlikely that use of different dose measures or interaction effects would result in changes of the magnitude already addressed in some of the sensitivity analyses. Third, even if there are such changes, there are likely to be countervailing responses; e.g., longer exposure periods may predict greater yield losses but O_3-water stress tends to dampen or reduce the yield estimates. Finally, it should be noted that potential improvements in economic estimates are policy-relevant only to the extent that they alter the relationship between total benefits and total costs of that policy. Uncertainties in other effects categories are probably greater.

In conclusion, the recent economic estimates of benefits to agriculture of O_3 control, particularly those estimates by Kopp et al. (1984) and Adams et al. (1984b), meet the general criteria discussed in Section 6.5 and hence provide the most defensible evidence given in the literature to date of the general magnitude of such effects. Relative to estimates given in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) and economic information on most other O_3 effects categories (non-agricultural), these two studies, in combination with the underlying NCLAN data on yield effects, provide the most comprehensive economic information to date on which to base judgments regarding the economic efficiency of alternative SNAAQS. As noted above, there are still gaps in plant science and aerometric data and a strong need for meteorological modeling of O_3 formation and transport processes for use in formulating rural O_3 scenarios. With regard to the economic data and models used, the impact of factors that upset free-market equilibria needs further analysis. Additionally, it must be emphasized that none of the studies has accounted for the compliance costs of effecting changes in O_3 concentrations in ambient air. For a cost-benefit analysis to be complete, the annualized estimated benefits to agriculture that would result from O_3 control would have to be combined with benefits accruing to other sectors and then compared with the overall annualized compliance costs.

6.8.10 Effects of Peroxyacetyl Nitrate on Vegetation

Peroxyacetyl nitrate (PAN) is a highly phytotoxic air pollutant that is produced by photochemical reactions similar to those that produce O_3. Both O_3 and PAN can coexist in the photochemical oxidant complex in ambient air. The effects of PAN were a concern in southern California for almost 20 years before the phytotoxicity of O_3 under ambient conditions was identified. The symptoms of photochemical oxidant injury that were originally described (prior to 1960) were subsequently shown to be identical with the symptoms produced by PAN. Following the identification of PAN as a phytotoxic air pollutant, PAN injury (foliar symptoms) has been observed throughout California and in several other states and foreign countries.

6.8.10.1 Factors Affecting Plant Response to PAN. Herbaceous plants are sensitive to PAN and cultivar differences in sensitivity have been observed in field and controlled studies. Trees and other woody species, however, are apparently resistant to visible foliar injury from PAN (Taylor, 1969; Davis, 1975, 1977).

Taylor et al. (1961) demonstrated that there is an absolute requirement for light before, during, and after exposure or visible injury from PAN will not develop. Field observations showed that crops growing under moisture stress developed little or no injury during photochemical oxidant episodes while, adjacent to them, recently irrigated crops were severly injured (Taylor, 1974).

Only a few studies have investigated the effects of PAN and O_3 mixtures on plants. When plants were exposed to both gases at their respective injury thresholds, no interaction between the gases was found (Tonneijck, 1984). At higher concentrations, the effects were less than additive. Studies with petunia confirmed that O_3 tended to reduce PAN injury (Nouchi et al., 1984).

6.8.10.2 Limiting Values of Plant Response. The limiting-value method has been used to estimate the lowest PAN concentration and exposure duration reported to cause visible injury on various plant species (Jacobson, 1977). The analysis yielded the following range of concentrations and exposure durations likely to induce foliar injury: (1) 200 ppb for 0.5 hr; (2) 100 ppb for 1.0 hr; and (3) 35 ppb for 4.0 hr.

Other studies, however, suggest that these values need to be lowered by 30 to 40 percent to reduce the likelihood of foliar injury (Tonneijck, 1984). For example, foliar injury developed on petunia plants exposed at 5 ppb PAN for 7 hr (Fukuda and Terakado, 1974). Under field conditions, injury symptoms may develop on sensitive species when PAN concentrations reach approximately 15 ppb for 4 hr (Taylor, 1969).

6.8.10.3 Effects of PAN on Plant Yield. Only a few limited studies have been conducted to determine the effects of PAN on plant growth and yield. In greenhouse studies, radish, oat, tomato, pinto bean, beet, and barley were exposed to PAN concentrations of up to 40 ppb for 4 hr/day, twice/wk, from germination to crop maturity (Taylor et al., 1983). No significant effects on yield were detected. This is supportive of field observations, in which foliar injury from ambient PAN exposures was found but no evidence was seen of reduced yield in these crops. In contrast, lettuce and Swiss chard exposed to PAN concentrations of up to 40 ppb for 4 hr/day, twice/wk, from germination to crop maturity showed yield losses up to 13 percent (lettuce) and 23 percent (Swiss chard) without visible foliar injury symptoms (Taylor et al., 1983). The results indicate that PAN at concentrations below the foliar-injury threshold can cause significant yield losses in sensitive cultivars of leafy vegetable crops. In addition, photochemical oxidant events have caused foliar injury on leafy vegetables (Middleton et al., 1950) for which the foliage is the marketable portion. After severe PAN damage, entire crops may be unmarketable or else extensive hand work may be required to remove the injured leaves before the crop may be marketed.

A comparison of PAN concentrations likely to cause either visible injury or reduced yield with measured ambient concentrations (see Chapter 5) indicates that it is unlikely that ambient PAN will impair the intended use of plants in the United States except in some areas of California and possibly in a few other localized areas.

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APPENDIX 6A

COLLOQUIAL AND LATIN NAMES OF PLANTS DISCUSSED IN THE CHAPTER

APPENDIX 6A. COLLOQUIAL AND LATIN NAMES OF PLANTS DISCUSSED IN THE CHAPTER

Colloquial Name	Latin name
Alfalfa	*Medicago sativa* L.
Ash	
Green	*Fraxinus pennsylvanica* Marsh.
White	*Fraxinus americana* L.
Aspen	
Bigtooth	*Populus grandidentata* Michx.
Azalea	
Delaware valley white	*Rhododendron mucronatum* Don.
Hinodegiri	*Rhododendron obtusum* Planch.
Korean	*Rhododendron poukhanensis* Leveille
Barley	*Hordeum vulgare* L.
Bean	*Phaseolus vulgaris* L.
var. - French	
Green snapbean	
Navy	
Pinto	
Red kidney	
Snapbean	
White	
Bean	
Broad	*Vicia faba* L.
Beet	*Beta vulgaris* L.
Garden	
Sugar	
Begonia	*Begonia semperflorens* Link and Otto
Begonia	*Begonia* X *hiemalis* Fotsch.
Birch	
White	*Betula papyrifera* Marsh.
Yellow	*Betula alleghaniensis* Britton
Cabbage	*Brassica oleracea capitata* L.
Carnation	*Dianthus caryophyllus* L.
Carrot	*Daucus carota* var. *sativa* DC.

APPENDIX 6A. (continued)

Colloquial Name	Latin name
Chard	
Swiss	*Beta vulgaris* var. *cicla* L.
Cherry	
Black	*Prunus serotina* Ehrh.
Chrysanthemum	*Chrysanthemum morifolium* Ramat.
Citrus	*Citrus* sp.
Clover	
Landino	*Trifolium repens* L.
Coleus	*Coleus blumei* Benth.
Corn	*Zea mays* L.
Field	
Sweet	
Cotoneaster	*Cotoneaster divaricata* Rehd.
Cotton	*Gossypium hirsutum* L.
Cottonwood	
Eastern	*Populus deltoides* Bartr.
Elder	
Black	*Sambucus nigra* L.
Elm	
Chinese	*Ulmus parvifolia* Jacq.
Endive	*Cichorium endiva* L.
Fir	
Douglas	*Pseudotsuga menziesii* (Mirb.) Franco.
Geranium	*Pelargonium hortorum* Bailey
Grape	*Vitis vinifera* L.
Grape	*Vitis labrusca* L.
Gum	
Black	*Nyssa sylvatica* Marsh.
Hemlock	
Eastern	*Tsuga canadensis* (L.) Carr.

APPENDIX 6A. (continued)

Colloquial Name	Latin name
Holly	
American	*Ilex opaca* Ait.
Japanese	*Ilex crenata* Thunb.
Larch	
Japanese	*Larix leptolepis* Gord.
Lettuce	
var.-Cos (Romaine)	*Lactuca sativa* L.
Linden	
American	*Tilia americana* L.
Locust	
Black	*Robinia pseudoacacia* L.
Maple	
Red	*Acer rubrum* L.
Sugar	*Acer saccharum* L.
Marigold	*Tagetes erecta* L.
Milkweed	*Asclepias syriaca* L.
Morning glory	*Ipomea nil* Roth.
Mountain laurel	*Kalmia latifolia* L.
Muskmelon	*Cucumis melo* L.
Mustard	*Brassica migra* (J.) Koch
Nettle (little leaf)	*Urtica urens* L.
Oak	
Black	*Quercus velutina* Lam.
California black	*Quercus kelloggii* Newb.
Willow	*Quercus phellos* L.
Oat	*Avena sativa* L.
Onion	
Australian	*Allium cepa* L.
Pasture grass	
Australian	*Phalaris aquatica*
Grasslands	*Dactylis glomerata* L.
Victorian	*Lolium perenne* L.

APPENDIX 6A. (continued)

Colloquial Name	Latin name
Peanut	*Arachis hypogea* L.
Pepper	*Capsicum annuum* L.
Petunia	*Petunia hybrida* Vilm.
Pine	
Austrian	*Pinus nigra* Arnold
Eastern white	*Pinus strobus* L.
Jeffrey	*Pinus jeffreyi* Grev. and Balf.
Loblolly	*Pinus taeda* L.
Lodgepole	*Pinus contorta* var. *murrayana* (Balf.) Critch
Monterey	*Pinus radiata* D. Don
Pitch	*Pinus rigida* Mill.
Ponderosa	*Pinus ponderosa* Laws.
Scotch	*Pinus sylvestris* L.
Shore	*Pinus contorta* var. *contorta* Dougl. ex Laud
Slash	*Pinus elliotti* Englem. ex Vasey
Sugar	*Pinus lambertiana* Dougl.
Table mountain	*Pinus pungens* Lamb.
Virginia	*Pinus virginiana* Mill.
Western white	*Pinus monticola* Dougl.
Poinsettia	*Euphorbia pulcherrima* Wildenow
Poplar	*Populus* sp.
Hybrid poplar	*Populus* X *euramericana*
Hybrid poplar	*Populus maximowiczii* X *trichocarpa*
Hybrid poplar	*Populus deltoides* X *trichocarpa*
Potato	*Solanum tuberosum* L.
Privet	
Amur	*Ligustrum amurense* Carr.
Radish	*Raphanus sativus* L.
Snapdragon	*Antirrhinum majus* L.
Soybean	*Glycine max* (L.) Merr.
Spinach	*Spinacia oleracea* L.
Spruce	
Sitka	*Picea sitchensis* (Bong.) Carr.
White	*Picea glauca* (Moench) Voss

APPENDIX 6A. (continued)

Colloquial Name	Latin name
Strawberry	*Fragaria chiloensis* var. *ananassa* Bailey
Sunflower	*Helianthus anuus* L.
Sweetgum	*Liquidambar styraciflua* L.
Sweet mock-orange	*Philadelphus coronarius* L.
Sycamore	
American	*Platanus occidentalis* L.
Tomato	*Lycopersicon esculentum* Mill.
Tree-of-heaven	*Ailanthus altissima* Swingle
Turfgrass	
Annual bluegrass	*Poa annua* L.
Bermudagrass	*Cynodon dactylon* L., Pers.
Colonial bentgrass	*Agrostis tenuis* Sibth.
Creeping bentgrass	*Agrostis palustris* Huds.
Kentucky bluegrass	*Poa pratensis* L.
Red fescue	*Festuca rubra* Gaud.
Red top	*Agrostis alba* L.
Ryegrass	*Lolium perenne* L.
Tall fescue	*Festuca arundinaceae* Schreb.
Zoysiagrass	*Zoysia japonica* Steud.
Turnip	*Brassica rapa* L.
Viburnun	
Tea viburnun	*Viburnum setigerum* Hance
Linden viburnum	*Viburnum dilatatum* Thunb.
Walnut	*Juglans nigra* L.
Black	
Wild strawberry	*Fragaria virginiana* Duchesne
Wheat	
Winter	*Triticum aestivum* L.
Yellow poplar (Tulip poplar)	*Liriodendron tulipifera* L.
Yew	*Taxus* X *media* Rehd.

APPENDIX 6B

SPECIES THAT HAVE BEEN EXPOSED TO OZONE TO DETERMINE DIFFERENTIAL RESPONSES OF GERMPLASM TO PHOTOCHEMICAL PRODUCTS

APPENDIX 6B. SPECIES THAT HAVE BEEN EXPOSED TO OZONE TO DETERMINE DIFFERENTIAL RESPONSES OF GERMPLASM TO PHOTOCHEMICAL PRODUCTS

Species	References
Alfalfa	Howell et al., 1971
Azalea	Gesalman and Davis, 1978
Bean	Butler and Tibbitts, 1979a,b Davis and Kress, 1974 Meiners and Heggestad, 1979 Heggestad et al., 1980
Begonia	Reinert and Nelson, 1979 *Adedipe, 1972*
Chrysanthemum	Wood and Drummond, 1974 Brennan and Leone, 1972
Cucumber	Ormrod et al., 1971
Eggplant	Rajput and Ormrod, 1976
English holly	Brennan and Leone, 1970
Forage legumes	Brennan et al., 1969
Grape	Richards et al., 1958
Lettuce	Reinert et al., 1972
Morning glory	Nakamura and Matsunaka, 1974
Oat	Brennan et al., 1964
Petunia	Feder et al., 1969 Cathey and Heggestad, 1972 Elkiey and Ormrod, 1981
Pine	Berry, 1971 Houston, 1974
Poplar	Karnosky, 1977
Poinsettia	Manning et al., 1972
Potato	Heggestad, 1973 DeVos et al., 1982

7. EFFECTS OF OZONE ON NATURAL ECOSYSTEMS AND THEIR COMPONENTS

7.1 INTRODUCTION

The responses of individual species and subspecies of agricultural plants to ozone (O_3) and peroxyacetyl nitrate (PAN) exposure were discussed in the preceding chapter. In addition, the responses of trees and other native vegetation to ozone were briefly discussed. The present chapter discusses the effects of O_3 stress on simple and complex plant communities to illustrate that such effects, because of the interconnections and relationships among ecosystem components, can produce perturbations in ecosystems. Stresses placed on biota and the ecosystems of which they are a part can produce changes that are long-lasting and that may be irreversible. Ecosystem responses to PAN are not discussed in this chapter since data dealing with the effects of PAN on ecosystems are virtually nonexistent, since trees and other woody plants appear to be resistant to PAN (Chapter 6), and since the occurrence of PAN at phytotoxic concentrations is believed to be a regional rather than a national problem.

Material in this chapter is organized into seven main sections that are presented in the following sequence: (1) overview and description of ecosystems; (2) description of responses to stress that are characteristic of ecosystems; (3) discussion of the effects of ozone on primary production in terrestrial ecosystems, including effects on the growth of trees and mechanisms involved in those effects; (4) discussion of the effects of ozone on other ecosystem components and their interactions; (5) discussion of the effects of ozone on specific forest ecosystems; (6) discussion of the effects of ozone on other ecosystems; and (7) a brief discussion on the economic valuation of ecosystems.

7.2 CHARACTERISTICS OF ECOSYSTEMS

An ecosystem is an integrated unit of nature consisting of interacting populations of plants and animals in a given area (the community) whose survival depends on the maintenance of biotic (living) and abiotic (nonliving) functions and interrelationships. The biotic components of ecosystems are: (1) producers, which are principally green plants that capture the energy of the sun through photosynthesis; (2) consumers, which utilize as their energy source the food produced and stored by the producers; and (3) decomposers, which obtain their energy by breaking down and converting dead organic matter into inorganic compounds and which release carbon dioxide to the atmosphere. The abiotic components include: air, water, the soil matrix, and inorganic substances. Temperature, radiation, barometric pressure, and other climatic factors are, along with pollution, additional abiotic factors affecting ecosystems (Billings, 1978; Odum, 1971; Smith, R., 1980).

An ecosystem usually has definable limits within which the integrated functions of energy flow, nutrient cycling, and water flux are maintained (Odum, 1969; Odum, 1971; Jordan and Medina, 1977). Some flow of energy and materials occurs, however, between adjacent ecosystems. Ecosystems are capable of responding to changes in the movement of energy and materials from adjacent environments as well as to changes in their own environment (Cox and Atkins, 1979). Ecosystems receive gases, nutrients, and the energy of the sun from their environment and utilize these; and, in turn, make their own contributions to the environment. Energy flows through the system unidirectionally and is dissipated into the atmosphere, while water, gases, and nutrients are usually recycled and fed back into the system. When materials are not returned through recycling, they must be obtained in another way. Plant and animal populations within the system represent the fundamental units through which the system functions (Smith, R. 1980); that is, through which energy is exchanged and nutrients are cycled (Smith, R., 1980; Billings, 1978; Odum, 1971). Any action that changes the flow of nutrients, energy, or both will cause a change in the relationships that exist between the environment and living organisms, as well as in the relationships among the organisms themselves.

The agricultural ecosystems discussed in Chapter 6 and the natural ecosystems discussed in this chapter possess the same basic functional components, require energy flow and mineral cycling for maintenance, and are subject to the dominating influences of climate and substrate. Natural ecosystems range from simple systems with few species to complex systems with many species. Their populations also vary in genetic composition, age, and species diversity. They are self-regulating and self-perpetuating. Agroecosystems, on the other hand, are monocultures of similar genetic and age composition, manipulated to maximize productivity; and they are unable to maintain themselves without the addition of nutrients, water, and human effort.

The differences in structure of natural and agroecosystems are significant in the context of responses to oxidant and other pollution stress. While the manipulation and maintenance of agroecosystems require human effort, the amenability of such monocultures to management means that the effects of air pollution stress can be partially overcome by such practices as selection of resistant cultivars, irrigation, and use of fertilizers. Natural ecosystems, on the other hand, generally are not amenable to management because of their species diversity and complexity. Natural ecosystems tend to respond more slowly than agroecosystems to perturbations such as air pollution; once perturbed, however, they may lose their capability for self-repair (Cox and Atkins, 1979).

The subtle and indirect effects of pollutant dosages on individual species can set the stage for changes in community structure that may possibly have irreversible consequences (Guderian and Kueppers, 1980). Increasing pollutant stress provides a selective force that favors some genotypes, suppresses others, and eliminates those species that lack sufficient genetic diversity to survive. Thus, the occurrence and distribution of plants are influenced; and community composition and species interactions are changed such that the basic structure of the ecosystem is ultimately changed (Treshow, 1980). This succession may take years, decades, or longer, depending on the pollutant concentration and dose and on the species involved.

7.3 CHARACTERISTIC RESPONSES OF ECOSYSTEMS TO STRESS

Ecosystems respond to ozone, as well as to other stresses, through the responses of the populations of organisms that compose them. In the responses of ecosystems to stress three main levels of interaction are involved: (1) between the individual and the environment, (2) between the population and its environment, and (3) between the biological community and its environment (Billings, 1978). Disturbances may have a positive effect or may produce both positive and negative responses. Responses at the ecosystem level are more diffuse and of longer duration than responses at the population level. Acute stresses that are followed by rapid recovery and return to an unstressed state may have a different effect on the ecosystem than chronic stresses that continue for some time. Stress at the community level requires the diversion of energy from growth and reproduction to maintenance. Thus, biomass accumulation tends to decrease as organisms attempt to cope with the disturbance. Decreased cycling and increased nutrient turnover frequently appear. Disturbance favors the development of communities dominated by small-bodied, rapidly reproducing species; and succession reverts to an earlier stage (Odum, 1985).

Studies around strong point sources of air pollution and radiation, along with results from laboratory and field experiments, as summarized by Smith (1981), suggest that ecosystems, especially forest ecosystems, respond to increasing pollutant stress in a predictable pattern that may be thought of as a continuum of responses (Bormann, 1985). The sequence of responses outlined by Bormann is given in modified form in Table 7-1 to assist in understanding

TABLE 7-1. CONTINUUM OF CHARACTERISTIC ECOSYSTEM RESPONSES TO POLLUTANT STRESS

Phase	Response characteristics
0	No response occurs. Manmade pollutants are absent or constitute insignificant stress. Plant growth occurs under natural conditions.
I	Ecosystems serve as sinks for pollutants. Species and/or ecosystem functions are relatively unaffected. Self-repair occurs.
II	Sensitive species or individuals are subtly and adversely affected. A reduction in photosynthesis, a change in reproductive capacity, or a change in predisposition to insect or fungus attack may occur.
III	Decline occurs in the populations with sensitive species; some individuals will be lost. Their effectiveness as functional members of the ecosystem diminishes. Ultimately, species could be lost from the system.
IV	Large plants, trees, and shrubs of all species die. The basic structure of the forest ecosystem is changed. Biotic regulation is affected as forest layers are peeled off: first trees, tall shrubs, and, under the most severe conditions, short shrubs and herbs. The ecosystem is dominated by weedy species not previously present and by small scattered shrubs and herbs.
V	The ecosystem collapses. The loss of species and changes in ecosystem structure, nutrients, and soil so damage the system that self-repair is impossible.

Source: Adapted from Bormann (1985).

the discussion that follows. While the effects on individual organisms begin at the molecular and physiological levels, as amply demonstrated for agricultural and other species in Chapter 6, the responses of ecosystems may be thought of as beginning at the organismal (individual) level and proceeding to the ecosystem level, as shown in Table 7-1.

7.4 EFFECTS OF OZONE ON PRIMARY PRODUCTION IN TERRESTRIAL ECOSYSTEMS

This section discusses the responses of individual plant species and other ecosystem components to explain how the disruption by ozone of plant processes at the organismal level can ultimately change structural patterns and such functional processes as energy flow, nutrient cycling, and biotic relationships in ecosystems. Of the ecosystems exposed to ozone and potentially affected by ozone, forest ecosystems are the largest and economically most important. Therefore, the respective components and processes of forest ecosystems have been studied more than those of other ecosystems and will be emphasized in the following discussion. Studies in which multiple trophic levels and interrelationships have been examined are presented in subsequent sections (Sections 7.5 and 7.6).

7.4.1 Effects of Ozone on Growth of Producers

Among the most important potential effects of ozone on terrestrial ecosystems is the reduction of primary production. In forest ecosystems, primary production is the addition of new organic matter to the ecosystem via photosynthesis in producers, i.e., trees and other green plants. Productivity is the most fundamental characteristic of an ecosystem. All the biological activity of a community depends on the energy from gross primary production. Forest productivity is higher than that of other ecosystems, and net productivity of 1200 dry g m^{-2} yr^{-1} (2.2 lb yd^{-2} yr^{-1}) for trees and shrubs combined is quite typical for temperate forests (Whittaker, 1965). Productivity is highly dependent on system age and environmental parameters, the most important of which are nutrient and water availability and temperature. Air quality also influences forest production in certain environments.

In forest ecosystems, tree populations play a critical role. As producers, trees influence the structure (species composition and trophic relationships) and energy flow and nutrient cycling of forest ecosystems (Ehrlich and Mooney, 1983). Although they are woody perennial plants, trees basically respond to ozone exposure in the same manner as agricultural crop species, which are chiefly herbaceous annuals. The same plant processes are affected (Chapter 6). Perennial plants, however, because they live longer, must cope with both short- and long-term stresses, the effects of which can be cumulative, lasting over the years, or can be delayed, not becoming apparent for many years. Likewise, effects can possibly be mitigated through short- or long-term recovery or replacements. These stresses can increase or decrease with the age of the forest stand. They can act independently, additively, synergistically, or antagonistically and can occur simultaneously or sequentially (Cowling, 1985). Ozone can be a predisposing stress that makes trees more susceptible to other stresses, such as low temperatures, insects, and fungi. A discussion of the effects of ozone on the growth of trees, because of their critical role, is the requisite first step in explaining the responses of forest ecosystems to ozone.

7.4.1.1 *Controlled Studies on Growth of Trees*. Data were presented in Chapter 6 on the concentrations and durations of exposure to ozone shown to produce reductions in growth of trees under controlled conditions. For example, as discussed in greater detail in Chapter 6, significant suppression in growth in height was observed by Kress and Skelly (1982) in seedlings of trees exposed to O_3 for 6 hr/day for 28 days: loblolly pine (*Pinus taeda* L.) (0.05 ppm), 18 percent; pitch pine (*P. rigida* Mill.) (0.10 ppm), 13 percent; American sycamore (*Platanus occidentalis* L.) (0.05 ppm), 9 percent; sweetgum (*Liquidambar styraciflua* L.) (0.10 ppm), 29 percent; green ash (*Fraxinus pennsylvanica* Marsh.) (0.10 ppm), 24 percent; willow oak (*Quercus phellos* L.) and sugar maple (*Acer saccharum* L.) (both at 0.15 ppm), 19 and 25 percent, respectively. Other investigators have reported similar results for other tree species exposed to ozone under other regimes (e.g., Dochinger and Townsend, 1979; Mooi, 1980; Patton, 1981; Kress et al., 1982). On the other hand, yellow poplar (*Liriodendron tulipifera* L.) and white ash (*F. americana* L.) exhibited significant growth stimulation, as measured by dry weight, when exposed to 0.05 ppm ozone (Kress and Skelly, 1982). In most instances, reductions in growth from exposure to ozone were not accompanied by foliar injury. Sweet gum was an exception.

Hogsett et al. (1985), using exposures that simulated ambient conditions, noted a reduction in growth in height, diameter, and root systems in two varieties of slash pine seedlings receiving chronic O_3 exposure. The seedlings were exposed to one of three regimes: (1) charcoal-filtered air; (2) an exposure profile with a daily 1-hr maximum of 0.126 ppm at around 2 p.m., a 7-hr (9 a.m. to 4 p.m.) seasonal mean of 0.104 ppm, and an integrated exposure of 155 ppm-hr (sum of hourly ppm > 0); or (3) a similar ozone exposure profile but with a daily 1-hr maximum of 0.094 ppm, a 7-hr seasonal mean of 0.076 ppm, and an integrated exposure of 122 ppm-hr. Both varieties of slash pine exhibited an increasing reduction in growth with increasing O_3 concentration. A significant reduction ($p<0.001$) in stem diameter occurred by day 112 for both O_3 treatments: 24 percent less than that of controls for 'ellottii' and 30 percent less for 'densa' at the lowest O_3 exposure; and 40 percent and 50 percent below control plants for 'ellottii' and 'densa,' respectively, at the highest O_3 exposure. Both O_3 exposures also caused significant reductions in growth in height ($p <0.001$). The most pronounced change was observed in the growth of roots, which in 'elliottii' was reduced 33 percent by day 21 at an integrated exposure of 29 ppm-hr, and 27 percent by day 56 with an exposure of 63 ppm-hr.

7.4.1.2 Field Studies on Effects of Ozone on Growth of Trees in Natural Habitats.

Studies of the effects of ozone on the growth of trees in their natural habitats have centered on several major forest ecosystems. While the consequences of growth effects in forest ecosystems are examined in Section 7.5, data on the effects of ozone on the growth of individual tree species in these ecosystems are briefly summarized here.

Mann et al. (1980) found injury to needles and decreased growth in white pine grown in a plantation on the Cumberland Plateau (near Oak Ridge, TN). These effects were associated by the authors with episodes of ozone at 1-hour-average concentrations >0.08 ppm. Levels of SO_2 and NO_x were below 0.1 and 0.2 ppm, respectively, throughout the growing season.

In a subsequent study of the same trees, McLaughlin et al. (1982) found reduced annual radial growth, which they also attributed to high concentrations of ozone. McLaughlin et al. (1982) divided trees into three sensitivity classes on the basis of needle color and length and duration of retention. A steady decline in annual ring increment of sensitive white pines was observed during the years 1962 through 1979. Reductions of 70 percent in average annual growth and 90 percent in average bole growth of sensitive trees, compared to the growth of tolerant and intermediate trees, were noted. Tolerant trees showed a consistently higher growth rate of 5 to 15 percent ($p = 0.005$) than intermediate trees for the 1960 to 1968 interval, similar growth from 1969 through 1975, and reduced growth of 5 to 15 percent (but significant only at $p = 0.10$) for the period 1976 through 1979 compared to trees of intermediate sensitivity. Needles of ozone-sensitive trees were 15 to 45 percent shorter than those of either of the other classes. Decline was attributed primarily to chronic exposure to O_3, which frequently occurred at phytotoxic concentrations in the area. For the years 1975 through 1979 the incidence rates for hourly concentrations $\geq$ 0.08 ppm were: 1976, 190 hr; 1977, >339 hrs; 1978, 190 hr; 1979, 125 hr. Maximum 1-hour concentrations ranged from 0.12 to 0.2 ppm during this period. The pollutants SO_2 and fluoride have been measured in the area, but the premature loss of needles and occasional tip necrosis of needles of the current year are manifestations usually associated with O_3 and no cause-and-effect relationship with SO_2 is indicated by the available data.

Benoit et al. (1982) studied the growth in annual rings of native eastern white pines of reproducing age to evaluate the possible effects of oxidant air pollution on the long-term growth of forest species in a region of the Blue Ridge Mountains of Virginia extending from the northern end of Skyline Drive in Shenandoah National Park to the southernmost portion of the Blue Ridge Parkway lying in Virginia. The three white pines in each study plot were classified as sensitive, intermediate, or tolerant, based on a foliar rating scale that incorporated needle length, needle retention by number of years, and the presence of typical O_3 symptoms on needles. The mean ages of ozone-tolerant, intermediate, and ozone-sensitive tree classes were 53, 52, and 56 years, respectively. From 1955 to 1978, growth in mean annual radial increment (tree ring growth) was 25 percent and 15 percent less than that of tolerant trees for sensitive and intermediate trees, respectively. Only the 25 percent decrease for ozone-sensitive trees, however, was significant ($p = 0.01$) (Table 7-2). Smaller mean increments in the last 10 years compared to the previous 24 years indicated a trend toward decline in overall growth rates in all classes of trees. A comparison of growth from 1974 to 1978 with that from 1955 to 1959 showed decreases of 26, 37, and 51 percent for tolerant, intermediate, and sensitive trees, respectively. The significant reduction in radial growth of O_3-sensitive white pines was assumed to be associated with cumulative stress resulting from the reduced photosynthetic capacity of oxidant-injured trees. At the time of this study, tree ring standardization methods

TABLE 7-2. ANNUAL MEAN RADIAL GROWTH INCREMENT, 1955 THROUGH 1978,[a] FOR THREE OZONE SENSITIVITY CLASSES OF NATIVE EASTERN WHITE PINES (*Pinus strobus* L.) GROWING IN TEN PLOTS OF THREE TREES EACH IN THE BLUE RIDGE MOUNTAINS IN VIRGINIA

(mm)

Plot	Tolerant trees[a]	Intermediate trees	Sensitive trees
1	4.59	2.13	3.08
2	3.52	2.12	2.86
3	8.19	6.34	6.89
4	4.80	3.75	2.62
5	5.94	6.53	5.73
6	4.64	3.76	2.62
7	2.85	2.75	1.51
8	3.91	4.52	1.96
9	3.32	2.04	2.61
10	1.67	2.98	1.46
Mean	4.34 A[b]	3.69 AB	3.10 B

[a] White pines rated tolerant, intermediate, or sensitive to O_3 based on foliar symptoms.

[b] Sensitivity classes with the same letter are not significantly different at p = 0.01 based on Duncan's multiple range test.

Source: Benoit et al. (1982).

had not been developed. In addition, the sample size of three trees per plot, in ten plots, was small.

The authors (Benoit et al., 1982) assumed that the reduction in radial growth was caused by O_3 because no significant changes had occurred in seasonal precipitation between the 1955-1963 and 1963-1978 periods. Increasing O_3 concentrations, therefore, could potentially account for growth reductions, especially since for the later period there was a negative correlation between precipitation and radial growth.

Sulfur dioxide concentrations were too low to have any vegetational effects. The monitoring of O_3 (Duchelle et al., 1983) indicated the presence of monthly average concentrations of 0.05 to 0.06 ppm on a recurring basis in the study area, with episodic peaks (1-hour) frequently in excess of 0.09 ppm. Episodes in the Blue Ridge Mountains lasting from 1 to 5 consecutive days have been reported by Skelly et al. (1984) (Table 7-3). Hayes and Skelly (1977)

TABLE 7-3. PEAK HOURLY OZONE CONCENTRATIONS IN EPISODES RECORDED AT THREE MONITORING SITES IN WESTERN VIRGINIA, SPRING AND SUMMER, 1979 THROUGH 1982 (ppm)

Date	1-hr O_3 concn., ppm Big Meadows	 Rocky Knob	 Horton Center
1979, April 11-12	0.100	0.128	N.A.[a]
1979, June 5-6	0.082	0.112	N.A.[a]
1979, September 12	0.095	0.079	0.072
1980, May 29-30	0.100	N.A.[a]	0.069
1980, June 13-15	0.093	0.088	0.063
1980, July 14-15	0.089	0.080	N.A.[a]
1980, July 31	0.102	0.113	0.129
1981, May 24	0.084	0.054	0.094
1981, June 22-23	N.A.[a]	0.106	0.073
1981, June 29-30	N.A.[a]	0.090	0.072
1981, July 8-11	0.096	0.129	0.114
1982, May 11-13	0.125	N.A.[a]	0.095
1982, May 16-17	0.090	N.A.[a]	0.085
1982, July 24-26	0.110	0.080	0.125
1982, July 27-28	0.090	0.080	0.110
1982, August 3-4	0.090	0.075	0.115
1982, August 19-20	0.095	0.065	0.090
1982, October 1-3	0.100	0.075	0.080

[a] N.A. = data not available.

Source: Skelly et al. (1984).

reported earlier that episodes in the area result from long-range transport of O_3 from urban areas. Fankhauser (1976) cited the transport of O_3 in a giant loop stretching from New York City, Philadelphia, Baltimore, and Washington, DC, through Virginia, West Virginia, and Ohio, and back to the Wheeling, WV - Pittsburgh, PA, area. This path continued for 4 to 5 days in September 1972. Another instance of O_3 transport occurred in May 1972, when a stagnant "high" and a slow-moving "low" transported air from the Chicago and Pittsburgh areas to Miami, FL.

In the studies discussed above (Mann et al., 1980; McLaughlin et al., 1982; Benoit et al., 1982), decline in vigor and reduction in the growth of coniferous trees were usually associated with the following sequence of events and conditions: (1) premature senescence and loss of older needles at the end of the growing season; (2) reduced carbohydrate storage capacity in the fall and reduced resupply capacity in the spring to support new needle growth;

(3) increased reliance of new needles on self-support during growth; (4) shorter new needles, resulting in lower gross photosynthetic productivity; and (5) higher retention of current photosynthate by foliage, resulting in reduced availability of photosynthate for external use (including repair of chronically stressed tissues of older needles) (McLaughlin et al., 1982).

Reported ozone concentrations such as those given above may not fully represent the exposures sustained by forest ecosystems in the Blue Ridge Mountains or in other mountainous areas, e.g., the San Bernardino Mountains in California (see Section 7.6.1). Several considerations are particularly important for assessing accurately the dose-response relationships reported for respective forest ecosystems, especially forest ecosystems at higher elevations: (1) the elevation(s) at which ozone-induced injury or damage has been observed; (2) the timing of peak ozone concentrations, i.e., during daylight or after dark; and (3) the possibility that transport trajectories and various meteorological conditions result in subjecting the forest, or parts of it, to multiple peak concentrations of ozone concentrations within a given 24-hr period. Discussions of the variation of ozone concentrations with altitude and of the occurrence of multiple peaks as the result of transport were presented in Chapter 5, but several important points must be noted here:

1. Sites at elevations above the nocturnal inversion layer (see Section 3.4.1 and Figure 3-4) can be exposed to higher peak and higher total concentrations of ozone than sites at lower elevations (see, e.g., Wolff et al., 1986; Miller and Elderman, 1977; Miller et al., 1982).

2. The maximum ozone concentrations observed at elevated, mountainous sites, as well as at many non-mountainous rural and remote sites, often occur at night (see e.g., Chapter 5; Lefohn and Jones, 1986; Wolff et al., 1986). For species in which the stomates remain fully or even partially open after dark, such as eastern white pine, this is particularly important.

3. Sites at higher elevations are often exposed to sustained or multiple peak concentrations of ozone within a given 24-hr period as the result of conditions such as (a) trapping inversions; (b) the successive transport of plumes from multiple urban source areas upwind, either aloft or across terrain devoid of sufficient ozone scavengers; and (c) the occurrence of mountain-valley and upslope-downslope flows, such that the trajectory of an air parcel passes back over the same forest or stand of trees (see Chapter 5).

In the forest studies reported above, only daytime ozone concentrations were monitored. Thus, the reported 1-hr and 8-hr ozone concentrations should be interpreted and used with caution since they may not represent either the number or the magnitude of the peak concentrations to which the forests were exposed.

7.4.1.3 Controlled and Field Studies on Growth of Other Native Vegetation. Little research has been done to determine the effects of O_3 on the growth of herbaceous plants in natural ecosystems except for the research of Harward and Treshow (1973), who studied the growth and reproduction of 14 understory species found growing in the Aspen zone in the western United States. Weights of both tops and roots of plants decreased with increasing concentrations when plants were exposed in portable plastic chambers to O_3 concentrations of 0.15 ppm or 0.3 ppm for 3 hr/day, 5 days/wk throughout the growing season. The most sensitive species showed injury in less than a week. Plants grown in ambient air containing O_3 concentrations of 0.05 to 0.07 ppm for 2 hr/day took 3 to 4 weeks to show injury symptoms, and the weights of both tops and roots of these plants were greater than those of plants exposed to the higher O_3 concentrations under controlled conditions.

Decreased vigor was associated with reduced root and top growth. Reduction in flower production and in the number and weight of seeds was observed in plants grown at 0.15 or 0.3 ppm O_3 (Harward and Treshow, 1973).

7.4.1.4 Mechanisms of Effects of Ozone on Growth of Producers. As discussed in Section 7.3, ozone has the potential for reducing the growth of green plants by inhibiting photosynthesis; by altering carbohydrate formation, allocation, and translocation; and by acutely damaging foliar tissue. In addition, genetic factors can attenuate or potentiate the growth response of trees and other green plants to ozone.

7.4.1.4.1 Reduction in Photosynthesis. Trees in which O_3 has been shown to reduce photosynthesis are northern red oak (*Quercus rubra* L.) (Reich and Amundson, 1985), loblolly pine (*Pinus taeda* L.), slash pine (*P. elliottii* Engelm. ex Vasey) (Barnes, 1972), ponderosa pine (*P. ponderosa* Laws) (Miller et al., 1969; Coyne and Bingham, 1981), eastern white pine (*P. strobus* L.) (Barnes, 1972; Yang et al., 1983; Reich and Amundson, 1985; Botkin et al., 1972), black oak (*Quercus velutina* Lamb), sugar maple (*Acer saccharum* Marsh) (Carlson, 1979; Reich and Amundson, 1985), and one poplar hybrid (*Populus deltoides* X *trichocarpa*) (Reich and Amundson, 1985) (also see Chapter 6). Two of these studies are presented in more detail here to demonstrate the role of ozone in reducing photosynthesis and the effects of reduced photosynthesis on growth.

Coyne and Bingham (1981) measured photosynthesis and stomatal conductance of attached ponderosa pine needles in relation to cumulative incident O_3 dose. Sapling trees in approximately even-aged (18 yr) stands in the forest, growing in similar environments, were studied. These trees had been exposed long-term to O_3 throughout their life history. Three chronic injury classes were identified (I, slight; II, moderate; III, severe) based on morphological O_3 injury symptoms. Differential photosynthetic and stomatal responses were correlated with the O_3 injury classification. Stomatal conductances were somewhat larger in the more O_3-sensitive trees (class III) during July and August, when needles were growing rapidly, than in Class I and II trees. The decline in photosynthesis and stomatal function normally associated with aging was accelerated as O_3 injury symptoms increased. Photosynthesis in all three injury classes was reduced to about 10 percent of the maximum rate observed in Class I current-year needles by incident exposures of approximately 800, 700, and 450 ppm-hr of ozone. Percentage inhibition was based on a comparison with the photosynthetic rates of new needles. Photosynthesis declined most rapidly in the sensitive trees (Class III). Photosynthetic rates were always higher in the trees with the fewest injured needles. Premature senescence and abscission of needles occurred soon after photosynthesis reached its lowest level. Losses in photosynthetic capacity in all trees and needle ages exceeded reductions in stomatal conductance, suggesting that injury to the mesophyll, carboxylation, or excitation of components of the CO_2 diffusion pathway was greater than injury to the stomata.

Reduced photosynthesis has also been observed in white pine. Yang et al. (1983) studied the effects of O_3 on photosynthesis in three clones of white pine with differing O_3 sensitivities (sensitive, intermediate, insensitive). Under controlled conditions, the clones were exposed to concentrations of 0.00, 0.10, 0.20, and 0.30 ppm ozone for 4 hr/day for 50 consecutive days. By day 10, photosynthesis in the sensitive plants exposed to 0.30 ppm was significantly reduced. By day 20, photosynthesis was reduced in sensitive plants exposed to 0.10, 0.20, or 0.30 ppm O_3. At the end of 50 days, net photosynthesis in the sensitive clone exposed to 0.10, 0.20, or 0.30 ppm was reduced from the control by 24, 42, and 51 percent, respectively. Photosynthesis in the intermediately sensitive clone was reduced by 6, 14, and 20 percent, respectively. The insensitive clone varied from the control at the 20-, 30- and 40-day periods, but had nearly recovered by 50 days. Decreased rates of photosynthesis were closely associated with visible needle injury, premature senescence, and reduction of biomass in the sensitive clones. Reduction in biomass was associated with the effect of O_3 exposure on the rate of photosynthesis, with plant metabolism, and with injury to the assimilatory apparatus of the plants.

7.4.1.4.2 Alterations in Carbohydrate Production and Allocation. Miller et al. (1969) found that exposure under controlled conditions of 3-year-old ponderosa pine seedlings to concentrations of 0.15, 0.30, or 0.40 ppm ozone 9 hr/day for 30 days reduced photosynthesis by 10, 70, and 85 percent, respectively. In addition, they noted that the reduction in photosynthesis was accompanied by decreases in the sugar and polysaccharide fractions of injured needles. Tingey et al. (1976) also observed that O_3 exposure differentially affected the metabolite pools in the roots and tops of ponderosa pine seedlings grown in field chambers. The amounts of soluble sugars, starches, and phenols tended to increase in the tops and decrease in the plant roots exposed to 0.10 ppm O_3 for 6 hr/day for 20 weeks. The sugars and starches stored in the tree roots were significantly less than those in the roots of the controls.

In the study by Mann et al. (1980) of white pine growing on the Cumberland Plateau (Section 7.4.1.2), differences in growth between sensitive and tolerant trees appeared to be caused by premature needle loss and retention of a reduced quantity of photosynthetically active tissue rather than by a reduction in the photosynthetic efficiency of the remaining foliage. In the McLaughlin et al. (1982) study of the same trees, the availability of less carbohydrate reduced the vigor of root systems and enhanced the susceptibility of the trees to root diseases. The loss in vigor of the trees was accompanied by reduced annual radial growth and a loss in the capacity to respond in years when conditions were favorable for growth. The primary cause of decline appeared to be exposure to high concentrations of O_3 and a sequence of events and conditions that led to premature senescence and loss of older needles, lower gross photosynthetic productivity, and reduced photosynthate availability for growth and maintenance of trees (McLaughlin et al., 1982). Carbon-14 transport patterns indicated that older needles were sources of photosynthate for new needle growth in spring and were storage sinks in the fall. The higher retention of ^{14}C-photosynthate by foliage and branches of sensitive trees indicated that the export of photosynthate to trunks and roots was reduced.

In native herbaceous plants, as in trees and cultivated crops (Chapter 6), O_3 inhibits the process of photosynthesis in sensitive plants and alters the distribution of carbohydrates from the leaves to other parts of the plant so that growth and reproduction are reduced. For example, in the study of native herbaceous plants by Price and Treshow (1972), grasses visibly injured by O_3 concentrations ranging from 0.15 to 0.25 ppm for as short as 2 hr exhibited a decrease in carbohydrate production, growth, and reproduction when given additional daily exposures.

7.4.1.4.3 *Foliar Leaching*. Krause et al. (1984), in West Germany, have associated limitations in growth of fir (*Abies alba* Mill), Norway spruce (*Picea abies* (L.) Karst), and certain hardwoods, e.g., beech (*Fagus sylvatica* L.), with foliar damage. They fumigated seedlings continuously for 6 weeks with O_3 concentrations that ranged from 0.07 to 0.30 ppm. Their studies indicated that the entrance of ozone into the leaf induced cell membrane damage in needles and leaves of the trees and resulted in the uncontrolled loss of nutrients. Leaching from the foliage was enhanced by high light intensity and low nutrient supply in soils. Membrane damage occurred in the absence of visible injury. The authors suggested that the loss of nutrients and reductions in photosynthesis, carbohydrate production, and root growth from O_3 injury causes trees to mobilize and translocate nutrient reserves from older needles to sites of greatest metabolic activity. Dieback then occurs because the growing tips of tree branches do not receive the nutrients and carbohydrates necessary for growth.

Taylor and Norby (1985) have pointed out that foliar leaching is a normal process and that according to Tukey et al. (1958) deleterious effects on metabolism are not observed if above-ground nutrient losses are rapidly replenished by root uptake. Furthermore, the rate of foliar leaching is accelerated by many stress factors in addition to air pollutants, such as water deficiency, temperature extremes, toxins, and mechanical damage (Tukey and Morgan, 1963).

7.4.2 Factors Modifying Effects of Ozone on Growth of Producers

7.4.2.1 *Genetic Factors*. The responses of individual plants or animals to ozone are partly the result of the genetic potential of each individual. Each population is a genetically diverse group of interbreeding individuals and the success of a population of plants or animals in any environment depends in part on its genetic diversity, that is, the presence of particular gene combinations and variations that give a species or taxon the capacity to adapt to environmental changes (Treshow, 1980). Plants in a given population (e.g., trees in a stand of eastern white pine) will not respond equally to O_3 exposure because of genetic diversity relative to the sensitivity of individual trees to ozone and because of the microenvironmental heterogeneity of the habitat. Some will be favored over others. Sensitive plants in a population die or are unable to compete with tolerant plants, and therefore do not reproduce. The tolerant plants reproduce and, in time, tolerant populations develop. The size and success of a population depend on the collective ability of organisms to reproduce and maintain their numbers in a particular environment. Those organisms that are tolerant of stress contribute most to future generations because they have the greatest number of progeny in the population (Woodwell, 1970; Odum, 1971; Smith, R., 1980; Roose et al., 1982). Tolerance refers to the relative ability of organisms of the same genetic composition (genotype) to maintain normal growth and remain free from injury in a given polluted environment. Tolerance is seldom complete, but is a matter of degree (Roose et al., 1982).

The studies described in Sections 7.4.1.2 (McLaughlin et al., 1982; Benoit et al., 1982) and 7.4.1.4 (Coyne and Bingham, 1981; Yang et al., 1983; Mann et al., 1980) have demonstrated that ozone sensitivity is not uniform even among individual plants of the same species. Differences in sensitivity to ozone are caused in part by differences in genetic potential.

In ponderosa pine, the response to O_3 may change with annual dose and climate. As observed by Miller and coworkers, 16.9 percent of ponderosa pine examined in field studies were classified as having slight injury in 1969 (Miller et al., 1969). By 1971, only 6.9 percent of the same trees were listed as having slight injury, but trees in the moderate injury category had increased from 15.6 to 20 percent (Miller, 1973). Based on the substantial shift of ponderosa pines from slight to moderate injury, Miller suggested that there may be no positive resistance to O_3. The continuing decline of the ponderosa pine populations studied appears to bear out this suggestion (Miller et al., 1982). The ability of this population to reproduce and compete with other populations has therefore decreased.

Changes in response to O_3 similar to those observed in ponderosa pines growing in their natural habitat have not been reported for eastern white pine, even though the studies of growth cited earlier show that populations of this species, like ponderosa pine, can also be divided into at least three classes of ozone sensitivity. Eastern white pine does not have the same role in eastern forest ecosystems as ponderosa pine has in western forest ecosystems.

Variability in response to O_3 has also been observed in a 2-year study of hardwood trees growing in urban habitats (Karnosky, 1981; 1983). Tree species were classified as tolerant, sensitive, or variable. Ozone-tolerant trees showed no visible symptoms during the 2-year study, but sensitive trees showed foliar symptoms. The sensitivity of a few species was highly variable; some individuals consistently showed foliar symptoms and others of the same species did not. Growth reductions, though postulated, were not measured (Karnosky, 1983).

As with many agricultural crops and some forest species, trees and other woody plants that are grown in a variety of urban habitats represent individuals that have been selected over time for viability in stressed environments. Umbach and Davis (1984) point out that trees obtained from commercial nurseries are not likely to represent the full range of genotypes present in the wild population of a species. The work of Rhoads et al. (1980), along with that of Karnosky (1981; 1983), suggests that, based on foliar injury, the majority of the plants growing along streets and in urban parks, arboreta, remnant woodlots, and suburban communities are relatively insensitive to O_3 exposure. Their relative insensitivity may be the combined result of genetic selection and physical factors affecting stomatal processes.

7.4.2.2 Other Factors. As described and documented in Section 6.3.2 of the preceding chapter, numerous factors influence the type and magnitude of responses of plants to ozone. The response of an individual plant to ozone will depend upon the physical and chemical environments of the plant and upon biological factors. Physical factors in the macro- and microenvironments of a plant that are known to modify the effects of ozone include temperature, relative humidity, light intensity, soil moisture, soil type, and soil fertility. Chemical factors known to modify plant response to ozone include other gaseous pollutants (e.g., SO_2), heavy metals (e.g., cadmium), nutrient deficiencies and excesses, and agricultural chemicals (e.g., pesticides, herbicides, chemical protectants).

In addition to genetic potential (Section 7.4.2.1 above), other biological factors can modify the response of trees to ozone. Such factors include the age of the plant and the developmental stage of both leaf and plant. For example, the age at which current foliage is most sensitive to O_3 varies among plant species. Conifer seedlings are susceptible to O_3 for a much longer period of time than many other plants. Susceptible conifer species were observed by Davis and Wood (1972), for example, to be most sensitive from 4 through 13 weeks after bud break. It should be noted, however, that physiological balances and the sensitivity of tree seedlings in chambers may be different from those of mature forest trees (McLaughlin, 1985). Woody shrubs and vines were most sensitive from 4 to 8 weeks after bud break (Davis and Coppolino, 1976). In both studies by Davis and coworkers, susceptibility of the plants to O_3 decreased as the growing season progressed. In contrast, azalea cultivars became more susceptible as the growing season progressed and retained their susceptibility into the fall (Davis and Coppolino, 1974). Thus, in conjunction with biological factors, the timing of exposures appears to modify plant response to ozone (see, e.g., Tingey et al., 1973).

As discussed in Section 6.3.2 of the preceding chapter, ozone occurs in conjunction with other stresses that also modify the productivity of an individual plant or of plant populations. Among the stresses to which trees are simultaneously exposed along with ozone are biotic pathogens and competition. Fungi and insects are by far the most important biotic stress factors in most forests (Cowling, 1985). The reader is referred to Section 6.3.2 (and Table 6-2) for references to studies on the interactions between ozone and plant diseases and insect pests in agricultural species and in some tree and ornamental species. Additional discussion on the effects of ozone on plant-pathogen and plant-insect interactions is presented in Sections 7.5 and 7.6 below.

7.5 EFFECTS OF OZONE ON OTHER COMPONENTS AND INTERACTIONS IN TERRESTRIAL ECOSYSTEMS

The ecosystem processes of energy flow and nutrient cycling are directly related to the plant physiological processes of photosynthesis, nutrient uptake, biosynthesis, respiration, and translocation. The alteration of these physiological processes is the fundamental cause of all other ecosystem effects. Data presented in Chapter 6 (Section 6.3) and in Section 7.4 above indicate that photosynthesis and the partitioning of photosynthate in the plant can be affected by exposure of the plant to ozone. The data presented also indicate that a sustained reduction in photosynthesis will ultimately affect the growth, yield, and vigor of a plant. Such data highlight the potential for ozone to reduce primary productivity. The effects of ozone on primary productivity have, in turn, potential consequences for entire ecosystems, since consumer and decomposer populations in ecosystems depend on the flow of energy from producers through the food chain.

Two fundamental processes in the food chain are photosynthesis and decomposition. Thus, the two groups of organisms particularly critical to the maintenance of an ecosystem are the producers, through which solar energy, carbon, and nutrients enter the biotic components of the ecosystem; and the decomposers, through which nutrients are released for reuse.

The following sections discuss the potential consequences for respective populations, processes, and interactions in ecosystems of ozone-induced responses in producers. Figure 7-1, derived from McClenahen (1984), shows how air pollution may be expected to affect forest ecosystems. Air pollutants may act as both predisposing and inciting stresses that influence trees. Predisposing stresses usually have a long-term role in weakening trees and thus making them more susceptible to inciting factors, which are short-term episodic stresses, such as insect defoliation, weather damage, or acute air pollution injury, that may abruptly alter tree physiology and increase the susceptibility of the tree to secondary biotic stresses (McLaughlin, 1985). In Figure 7-1, it is clear that the impact of air pollutants is sequential but also cyclic; that is, effects on individual organisms eventually find expression as effects on the ecosystem, with ecosystem changes producing, in turn, effects on individual organisms.

7.5.1 Producer-Producer Interactions: Competition and Succession

According to Ehrlich and Mooney (1983), in forest ecosystems, trees are the producers that serve as the controller organisms of the ecosystem; that is, they are the organisms that determine the species composition and trophic relationships of the ecosystem. Unless they are the result of a specific biotic disease or an acute pollutant exposure, injuries and disturbances to trees are cumulative and are frequently the culmination of a number of chronic stresses. Injury to or disturbance of tree species, whether from air pollution or other stresses, starts the retrogressive successional processes that could

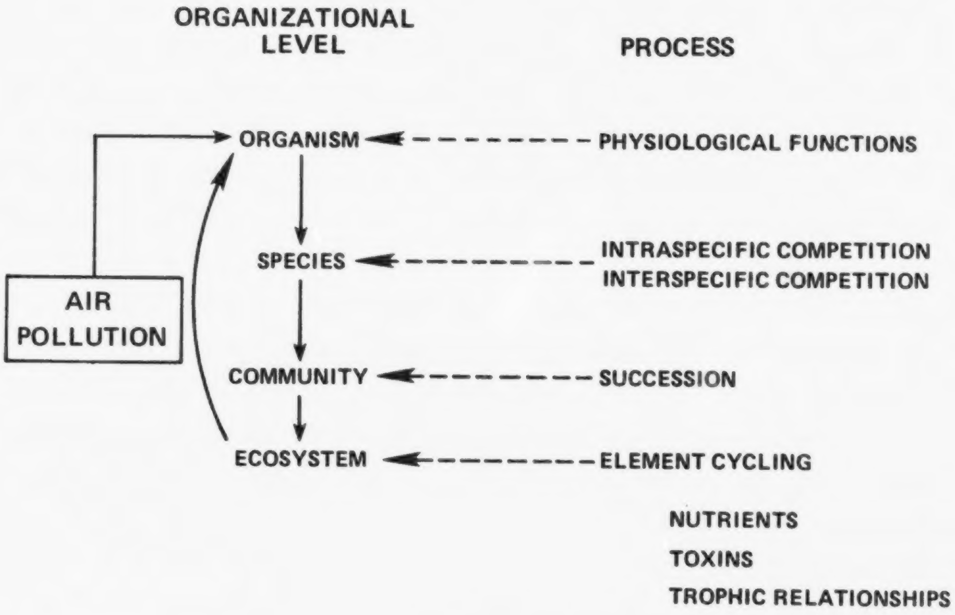
ORGANIZATIONAL LEVEL
PROCESS
ORGANISM
PHYSIOLOGICAL FUNCTIONS
SPECIES
INTRASPECIFIC COMPETITION
INTERSPECIFIC COMPETITION
AIR POLLUTION
COMMUNITY
SUCCESSION
ECOSYSTEM
ELEMENT CYCLING
NUTRIENTS
TOXINS
TROPHIC RELATIONSHIPS

Figure 7-1. Pathways of air pollutant impact in forest ecosystems.

Source: McClenahen (1984).

ultimately lead to the loss of the ecosystem (see Table 7-1, Phases II through V; Bormann, 1985).

In most ecosystems, the principal interaction among species is competition for resources. Producer species compete with one another for the limited resources of space, light, water, and minerals (Billings, 1978). Those producer species and populations best able to utilize the resources available survive and replace those that previously occupied the area. A gradual orderly change in community composition called succession occurs over time as dominant plants change and as new communities arise, develop, and mature. Succession is characterized by a shift from annual species through biennial and perennial herbs to woody shrubs and trees, and changes in the woody species over time. Each successive community is related to the one that preceded it. In time, communities arrive at some form of steady state and are more or less self-maintaining as long as abiotic factors remain constant. Through succession, ecosystems achieve the most stable state possible within the constraints of the environment (Odum, 1971; Cox and Atkins, 1979; Smith, R. L., 1980). Along with other abiotic factors, air pollution can affect the direction of succession by injuring the sensitive plant species.

In forest ecosystems, trees represent the later stages of succession and are adapted for high competitive ability (Brown, 1984). In the early stages of ecosystem development, however, competition by grasses and other herbaceous vegetation is very important. Competition among broad-leaved and needle-bearing trees is keen in mixed forest stands, especially in the later stages of stand development. Competition-induced mortality is an important feature of all planted and naturally regenerated forests. In fact, in most forests, more trees will die because of competitional stresses than all other stresses combined. Only a few trees survive to maturity (Cowling, 1985).

Ozone stress is an additional factor affecting growth and species composition and succession in forests and other plant communities in both the western and eastern United States. Ozone exerts selection pressure on sensitive species by causing their demise or by weakening them and making them less able to compete. Ozone-tolerant species may replace them in the plant communities. Disruption of food chains and modification of the rates of nutrient cycling resulting from species changes may result in a less stable community. Injury to, or disturbance of, the dominant tree species may return succession to an earlier stage (Woodwell, 1970; Bormann, 1985).

McClenahen (1978) has provided quantitative data on the impact of polluted air on the various strata and the composition of a forest ecosystem exposed to effluents from point sources of air pollution for nearly 40 years. In stands situated along a gradient of polluted air containing elevated concentrations of chloride, sulfur dioxide, and fluoride (photochemical oxidants were not monitored), overstory, subcanopy, shrub, and herb strata were analyzed for pollution effects.

A shift in the species composition of forest stands occurred on the sites investigated and was related to the pollution gradient. The density of overstory and herb layers was also correlated with the gradient. In the herb layer, an increase occurred in light-tolerant species that was an indirect effect of air pollution, resulting from the reduced overstory density. Light-tolerant species composed 68 percent of the total in areas of high pollution compared to 34 percent in areas of low pollution (McClenahen, 1978). Although concentrations of O_3 were not reported, the study illustrates how pollutant mixtures typical of some ambient conditions can change the species composition of forested areas by weakening trees in a population and thus lessening the ability of that population to compete. The changes observed were consistent with the first four phases of ecosystem response outlined in Table 7-1 (Bormann, 1985).

The modifying role of intra- and interspecific competition must be evaluated when studying long-term responses of forest communities to high O_3 concentrations (Taylor and Norby, 1985). Simulations of community dynamics in a pollutant-stressed forest in the southern Appalachian Mountains and in the eastern deciduous forest of North America after removal of the American chestnut [Castanea dentata (Marsh.) Borkh.] suggest that growth rates for certain tree species were significantly modified by competition. These simulations also suggest that in forests of mixed species with uneven-aged stands the subtle long-term responses are likely to be shifts in species composition rather than widespread degradation (West et al., 1980; cited in Taylor and Norby, 1985).

The effects of competition as a modifying factor in the responses of forest ecosystems to pollutants (e.g., ozone) are not unidirectional. Just as ozone is thought to modify the competitive ability of a species through its effects on sensitive individuals of that species, competitive stress may also modify responses of individuals to ozone. As McLaughlin (1985) has stated, ..."competitive stress, "..." in wellstocked forest stands, may have significant influence as either a predisposing or contributing factor in tree responses to anthropogenic stress."

Competition increases selection for resistance under polluted conditions and selection against resistance under less polluted conditions. Studies on plant responses to heavy metals and herbicides indicate that resistant populations develop, but that once the stress is removed the pollutant-resistant plants tend to decline in number (Roose et al., 1982). This evidence is corroborated by observations of ecosystems functioning under specific natural conditions. Certain terrestrial ecosystems require a major disturbance (e.g., fire, drought, and windstorms) to retain their characteristics (Vogl, 1980; Smith, W. H., 1980). In the absence of disturbance, some ecosystems appear to degrade, lose nutrients, become less productive, and have fewer species with a smaller biomass (Woodwell, 1970; Gorham et al., 1979).

Acute injury from air pollution resembles that from herbicides in that selection for resistances tends to be episodic. Chronic air pollution more closely resembles contamination of soil by heavy metals in that plants experience the polluted environment for a considerable portion of their lives. Resistance in either situation depends on the presence of the resistant or tolerant genotype in the plants that are growing in unpolluted air (Roose et al., 1982).

Annual plants in a forest ecosystem under selection pressure from air pollution and pollution-related stresses are capable of altering the genetic composition of the population each year through sexual reproduction until a stable population adapted to the stresses develops (McClenahen, 1978). As noted in Section 7.4.1, forest trees and shrubs, which are perennial plants, must cope with the cumulative effects of both short- and long-term stresses. The response of trees to stress may appear rapidly, for example, as when sensitive eastern white pine needles show visible evidence of exposure to episodic, high O_3 concentrations. In other instances, however, responses are often subtle and may not be observable for many years as trees adapt and their response to stress is expressed in differential growth resulting from changes in carbon allocation (Waring and Schlesinger, 1985; McLaughlin and Shriner, 1980), such as those induced when O_3 affects photosynthesis. Changes in growth patterns of ponderosa, Jeffrey, and eastern white pine trees have been attributed to stress resulting from O_3 exposures that began 15 to 20 years earlier (Miller and Elderman, 1977; Miller et al., 1982; McLaughlin et al., 1982; Benoit et al., 1982). Dendroecological studies of the dieback and decline of red spruce (Picea rubens Sarg) in the northeast (Johnson and Siccama, 1983) and of reduced growth rates of red spruce, balsam fir [Abies balsamea (L.) Mill.], and Fraser fir [A. fraseri (Purshl) Poir.] in central West Virginia and western Virginia (Adams et al., 1985) also provide further evidence that the reductions in growth and mortality measurable today probably began at least 20 years ago. Currently, there is no agreement as to the trigger factor that precipitated the dieback, mortality, and decreased growth, but multiple stresses, including air pollution, have been suggested (Johnson and Siccama, 1983; Adams et al., 1985). Ecosystem responses to these stresses usually are observable only after long periods of time.

According to Whittaker (1965), productivity (carbohydrate production) of a species appears to be the best predictor of the relative importance of that species in an ecosystem. When assessing the responses of forest ecosystems to O_3, the consequences of the loss of a particular plant species should be evaluated accordingly. This criterion explains why the loss of ponderosa pine in the San Bernardino Forest has had a greater impact than the loss of sensitive eastern white pine in the Appalachian Mountains. Their roles in the respective ecosystems are not of equal importance.

Studies of successional changes in specific ecosystems exposed to ozone are described in Sections 7.6 and 7.7 below. Data presented there indicate the potential for the occurrence of ozone-induced changes in composition and in successional patterns in forest and other ecosystems (see, e.g., Cobb and Stark, 1970; Miller, 1973; Harward and Treshow, 1973; Miller and Elderman, 1977; Miller et al., 1982).

7.5.2 Producer-Symbiont Interactions

7.5.2.1 Mycorrhizal-Plant Interactions. The roots of most plants growing under natural conditions are invaded by fungi and transformed into mycorrhizae or "fungus roots." The host plant and the fungus live together in an association that is generally beneficial to both organisms. The morphology of the root is modified, and as long as a balanced relationship is maintained no pathological symptoms occur (Gerdemann, 1974). Most plants, including important forest and horticultural species, could not reach maximum growth rates without mycorrhizae. Mycorrhizal fungi increase the solubility of minerals, improve the uptake of nutrients for host plants, protect roots against pathogens, produce plant growth hormones, and move carbohydrates from one plant to another (Hacskaylo, 1972). The mycorrhizal fungi in turn obtain food from the host.

This fungus-plant relationship is particularly important to plants growing on nutrient-poor soils.

Ozone may disrupt the association between the mycorrhizal fungi and host plants, possibly by inhibiting photosynthesis and reducing the amounts of sugars and carbohydrates available for transfer from the leaves to the roots. Carbohydrate partitioning is altered in plants exposed to ozone (Section 7.4.1.4 and Chapter 6) to the degree that certain plant organs (e.g., roots) may be deprived of photosynthate. In Chapter 6, the effects of ozone on root-to-shoot ratios were documented for agricultural species, demonstrating that ozone can affect root systems. Translocation may be reduced in ozone-stressed plants and thus deprive the mycorrhizal fungus of the amount of photosynthate needed to satisfy mycorrhizal requirements. The result would be reduced effectiveness of the mycorrhizal fungi (McCool and Menge, 1983).

Mycorrhizae are sensitive to the photosynthetic capacity of the host and the capacity of the host to translocate carbon compounds to the roots (Hacskaylo, 1973). For example, when seedlings of Virginia pine (Pinus virginiana Mill.), inoculated with the mycorrhizal fungus, Thelephora terrestris, and growing under a 16-hour photoperiod, were switched to 8-hour photoperiods, the seedlings became dormant within 4 weeks. No further invasion of rootlets by the fungus occurred even though root growth continued. Fungal sporophores were formed on the seedlings that remained under the 16-hour photoperiod. Studies have shown that simple sugars provided by plant roots are readily utilized by mycorrhizae and enhance fungal inoculation (Hacskaylo, 1973; Krupa and Fries, 1971).

Several studies of the effects of ozone on root and mycorrhizal systems have been reported. In a controlled study, Mahoney et al. (1982) found evidence that the mycorrhizal association of loblolly pine seedlings was not impaired by exposure to 0.07 ppm of O_3 plus 0.06 ppm of SO_2 for 6 hr/day for 35 days; however, a 12 percent decrease in dry weight of shoots was observed. In an earlier controlled study, McCool et al. (1979) demonstrated that infection of citrange (a citrus hybrid) by Glomus fasciculatus, an endomycorrhizal fungus, was decreased by exposure to 0.45 ppm ozone for 3 hr/day, 2 days/wk over 18 weeks. In the field, Berry (1961) examined the relationship of root condition and root fungi to emergence tipburn, i.e., ozone injury. Sampling of trees indicated the occurrence of almost twice the percentage of living feeder roots on healthy trees as on ozone-injured trees. The observations by Berry were made on trees in a forested valley in eastern West Virginia, and on trees in eastern North

Carolina, where ozone concentrations as high as 0.22 ppm for short durations (~1 hour), as measured by Mast meter, were observed in 1962 and where 4-hour average ozone concentrations in 1961 ranged from 0.03 to 0.065 ppm (Berry and Ripperton, 1963; Berry, 1964).

In the San Bernardino forest in California, Parmeter et al. (1962) observed that the feeder rootlet systems of ponderosa pines exposed to ozone showed marked deterioration. The number of mycorrhizal rootlets was decreased and many had been replaced by saprophytic fungi in stressed trees. (Information on ozone/oxidant concentrations in the San Bernardino forest is given in Section 7.6.)

Mycorrhizae assist in protecting conifer roots from pathogens such as Heterobasidion annosum (syn. Fomes annosus) (Krupa and Fries, 1971). Injury to the mycorrhizae or reduction in the number of mycorrhizae, such as can be induced by ozone exposure, can remove this protection. Non-mycorrhizal and mycorrhizal root systems contain essentially the same major volatile compounds; however, studies using Scots pine (Pinus sylvestris L.) indicate that the concentrations of monoterpenes and sesquiterpenes increase twofold to eightfold in roots infected by mycorrhizae. Many of the monoterpenes identified in mycorrhizal root systems are constituents of the oleoresins commonly found in conifers. Oleoresins play an important role in the resistance of wood to decay fungi (Rishbeth, 1951). Volatile oleoresin components from ponderosa pine have been shown to inhibit the growth of H. annosum and four Ceratocystis species (Cobb et al., 1968), and are believed to aid in defense of trees from bark beetles (Stark and Cobb, 1969). James and coworkers associated decreased oleoresin exudation with increased susceptibility to infection by H. annosum in roots (James et al., 1980a) and cut stumps (James et al., 1980b) of ponderosa and Jeffrey pines.

7.5.2.2 Bacterial-Plant Interactions. Ozone has also been shown to influence bacterial symbiosis in herbaceous species. Whether it does so in trees and woody shrubs has not been investigated. In herbaceous species, the rate of nitrogen fixation by symbiotic bacteria is dependent on the rate of photosynthesis by the plant. Symbiotic nitrogen fixation is the major bological source of fixed nitrogen (Tingey and Blum, 1973). Blum and Tingey (1977) found reduced root growth and reduced nodulation of soybeans (Glycine max (L.) Merr cv. Dare) by the bacterium Rhizobium japonicum when plant tops were exposed to O_3. No growth reductions occurred when the plant tops were protected from exposure to O_3 (Blum and Tingey, 1977). In an earlier study (Tingey and Blum, 1973), nodule number, nodule weight per plant, root growth, and leghemoglobin content per plant were all reduced by a 1-hr exposure to 0.075 ppm O_3. The reductions were associated with reduced photosynthetic capacity and less photosynthate for translocation to the roots. In a separate study, ladino clover (Trifolium repens L. cv. Tillman) was treated with filtered air, 0.3 ppm (588 $\mu g/m^3$) of O_3, or 0.6 ppm (1176 $\mu g/m^3$) of O_3 for two 2-hr exposures, one week apart, in controlled environment chambers (Letchworth and Blum, 1977). Plants of various ages were treated. Ozone reduced the growth and nodulation of test plants. The influence of O_3 varied with gas concentration and plant age.

7.5.3 Producer-Consumer Interactions

Consumers (heterotrophs) are organisms that feed on other organisms and constitute all trophic levels above the first. Production (energy storage) by consumers is termed secondary production. Consumers are extremely diverse, ranging in size from single-celled microscopic forms to large mammals. Only a limited amount of information on their response to pollutants is available (Newman, 1979; Alstad et al., 1982) despite the importance of the role of consumers, especially insects, in ecosystems. The influence of oxidants on these organisms is assumed to be chiefly through the food web. Few studies have been conducted to determine whether ozone has a direct impact on the organisms themselves.

The effects of ozone on producer-consumer interactions that have been observed may be secondary; that is, ozone may alter producer-consumer interactions by predisposing trees in a forest ecosystem to attack by predatory beetles and fungal pathogens. In addition, an unhealthy tree has less energy available to transfer through the food web so that the relationship among consumers in the food web is changed. Any mature natural community transfers 10 to 20 percent of the energy fixed by plants to herbivores (Woodwell, 1974). Disruption of photosynthesis and subsequent carbon allocation for vegetative and reproductive growth can decrease the amount of food available to other trophic levels in the food web and thus alter the movement of energy and nutrients through an entire system. The possibility of such alterations in response to stress from ozone is consistent with theory but such ozone-induced changes have not been demonstrated.

Invertebrate consumer populations such as insects may be subject to the influence of oxidants on their host or on their habitat. Insects are among the most important heterotrophic groups in ecosystems. The insect-plant relationship is a close one throughout succession. Changes in the plant community are soon followed by changes in the insect community. Herbivorous insects may play a key role in succession (Brown, 1984). While consistent with ecological theory, such changes as the result of ozone stress are again conjectural. The data available on the effects on insects of pollutants in general, and the effects of ozone in particular, are meager and are disproportionate to the importance of insects in forest ecosystems.

The review by Alstad et al. (1982) cites the work of Levy and coworkers (Levy et al., 1972; 1974), in which three species of Diptera were exposed to ozone. Prolonged fumigations with high concentrations of ozone, well above ambient air levels, inhibited egg hatching but no differences were observed between controls and exposed insects during the larval and pupal stages. Adults fumigated with ozone showed stimulation of ovipositon, an increase in the number of eggs laid, and an increase in the adult population (Levy et al., 1972). None of these effects were seen in ozone-exposed cockroaches or fire ants (Levy et al., 1974).

In contrast to the evidence for possible direct effects of ozone on insects, the evidence for indirect effects of ozone on insects (herbivores) is stronger, and indicates that effects on producers can result, for example, in increases in bark beetle infestation (see Section 7.6). Bark beetles are the most damaging and economically significant insect pests of commercially important conifers in the United States (Stark and Cobb, 1969). Beetle outbreaks in western forests are associated with several predisposing factors. These include host weakening caused by photochemical oxidants; root disease initiated by the fungi *H. annosum* or *Verticicladiella wagenerii* (Stark and Cobb, 1969); insect defoliation, such as pine looper stripping of ponderosa pine (Dewey et al., 1974); and various climatic stresses, such as drought and windthrow (uprooting and breakage by strong winds) (Rudinsky, 1962).

The only evidence of an effect of ozone on mammalian species of forest ecosystems is some evidence from studies of the San Bernardino forest ecosystem. Reductions in fruits and seeds in that ecosystem appear to be one of the effects of ozone-related stress in producers and data indicate that such reductions may be affecting the populations of small mammals. Fruits and seeds make up the largest part of the diet of most of the small mammals in mixed conifer forests. This is particularly true for the deer mouse (Peromyscus sp.), harvest mouse (Reithrodontormys sp.), chipmunk (Etuamias sp.), ground squirrel (Callospermophilus sp.), and western gray squirrel (Sciurus griseus anthonyi Mearns). Alterations in availability of seeds and fruits can alter the habitats and reproduction of these rodents (Taylor, 1973).

A trapping program at vegetation plots differentially impacted by chronic oxidant dose indicated that the same species were present when compared with results from trappings made 70 years ago (Kolb and White, 1974). Population numbers, however, appeared to be lower in comparison with other similar forest systems. Some evidence suggests that the size and frequency of acorn crops from California black oak may be smaller in areas receiving the greatest seasonal oxidant exposure (Miller et al., 1980). Reduced acorn availability could have an impact on small mammal populations.

Small mammals are important members of coniferous ecosystems because they are primary vectors of spore dissemination for hypogeous mycorrhizal fungi. Mammalian mycophagists spread the spores of the fungi necessary for the survival and health of conifers (Maser et al., 1978). Thus, changes in the structure and species composition of a forest will not only have an impact on the small mammal population, but also on the hypogeous fungi and therefore on whether coniferous species return to an ecosystem.

7.5.4 Producer-Decomposer and Producer-Pathogen Interactions

Decomposers are organisms such as litter-feeding invertebrates, bacteria, fungi, and protozoa (Smith, R. L., 1980) that are capable of degrading complex compounds and utilizing some of the decomposition products as their own food source while releasing inorganic substances (e.g., essential elements such as calcium, phosphorus, and magnesium) for use by other organisms.

Generally, one-third or more of the energy and carbon fixed annually by producers during photosynthesis in the forests is contributed to the forest floor as litter (mostly leaves) (Ovington, 1957). The reservoir of energy and mineral nutrients represented by litter is a very important resource in natural ecosystems since the growth of new green plants depends on the release of nutrients by decomposer organisms. In agroecosystems, litter is often removed or burned and fertilizer is added to the soil to replace the nutrients lost.

In a conifer forest, however, litter production and decomposition release approximately 80 percent of the annual mineral uptake, with the remainder retained in the living parts of the trees (Millar, 1974).

Needles on conifers usually persist for more than one year. Ozone causes premature senescence and the loss of older needles at the end of a growing season; and by reducing photosynthetic productivity, ozone decreases the amount of carbohydrates in the needles. The early loss of needles interferes with the decomposition process because the succession of fungi that normally takes place does not occur when needles drop off. Though most decomposition occurs on the forest floor, pine needles are invaded by fungi several months before needles are shed (Stark, 1972).

Bruhn (1980) has investigated the effects of oxidants on needle microflora population dynamics of pine in the San Bernardino National Forest. The decomposition of litter consisting of O_3-stressed needles was concluded to be more rapid. The taxonomic diversity and population density, however, of fungi that colonized living needles and later participated in decomposition were both reduced by O_3 injury as the normal increase with age was blocked by premature needle senescence and abscission. The author concluded that this alteration in microflora could weaken the stability of the decomposer community.

Decomposition occurs on the forest floor, even though pine needles are infected by decomposer fungi prior to needle drop. Thus, the effects of ozone and other oxidants on most of the decomposition process and on decomposers themselves remain uncertain in natural habitats. Although the occurrence of rapid fluxes of ozone to soil surfaces and the forest floor has been reported (National Research Council, 1977), documentation for the occurrence of such events is poor.

In Chapter 6, documentation is provided for the interactions between ozone-exposed plants and their pests. As noted in that chapter, ozone may inhibit or stimulate infection of plants by pathogens; and ozone may modify the success of other plant pests, either directly through effects on the invading organisms or indirectly through modification of the host plants. It is also possible that complex plant-insect or plant-pathogen interactions may alter the sensitivity of the plant to ozone. Studies showing modifications of plant disease by ozone in ornamentals and trees were tabulated in Chapter 6 (Table 6-2). None of the studies cited showed modification of ozone injury by infection with plant pathogens.

In a field study in the Blue Ridge Mountains of Virginia, Skelly (1980) found an increased incidence of root disease from Verticicladiella procera in oxidant-injured eastern white pines. Costonis and Sinclair (1972) found that Lophodermium pinastris and Aureobasidium pullulans were the fungi more commonly collected from eastern white pine foliage showing ozone injury. When trees were inoculated in conjunction with exposure to 0.06 to 0.1 ppm ozone for 4.5 hours, however, no evidence of additive or interactive effects was found (Costonis and Sinclair, 1972).

Only a few studies have reported on the effects of ozone in combination with other pollutants on disease development in woody species. Weidensaul and Darling (1979) inoculated Scots pine (Pinus sylvestris L.) seedlings with the fungus, Scirrhia acicola, 5 days before or 30 minutes following fumigation for 6 hours with 0.20 ppm SO_2, 0.20 ppm O_3, or both gases combined. Significantly more brown-spot lesions were formed on seedlings fumigated with SO_2 alone or SO_2 combined with O_3 than on controls when inoculation was done 5 days before fumigation. When inoculation was done 30 minutes after gas exposure, seedlings exposed to SO_2 alone had more lesions than those exposed to O_3 alone or O_3 combined with SO_2, but the numbers of lesions did not differ significantly between fumigated seedlings and controls. The authors concluded that ozone-induced stomatal closure may have been responsible for the latter observation.

As the results of the above studies indicate, the outcome of a pollutant-plant-pathogen interaction depends on the particular plant and pathogen involved and is also modified by environmental and ozone-exposure conditions. Laurence and Weinstein (1981) have emphasized the critical importance of examining multiple pollutant effects and the interactive effects of air pollutants with pathogens and insects in determinations of growth impacts. Likewise, Manion (1985) has emphasized the necessity of taking non-pollutant stresses, both biotic and abiotic, into account when attempting to attribute changes in forest ecosystems to air pollutants. Ecosystem responses will always be the integration of multiple stresses acting over time and space on diverse populations (see, e.g., Manion, 1985; Cowling, 1985; Smith, 1985; Prinz, 1985).

Whether ozone has direct or only indirect effects on plant infection by pathogens or on the course of the disease is unknown. The data of Hibben and Stotsky (1969), however, are illustrative of the fact that the dose of ozone required for direct effects on fungi, for example, may be much higher than ambient concentrations. These investigators examined the response of detached spores on agar of 14 fungi (none of them forest species) to 0.1 to 1.0 ppm of O_3 for 1, 2, and 6 hr. The large pigmented spores of *Chaetomium* sp., *Stemphylium sarcinaeforme*, *S. loti*, and *Alternaria* sp. were not influenced by 1.0 ppm of O_3. Germination of *Trichoderma viride*, *Aspergillus terreus*, *A. niger*, *Penicillium egyptiacum*, *Botrytis allii*, and *Rhizopus stolonifera* spores was reduced by O_3 exposure, but usually in concentrations above 0.5 ppm, though occasionally by doses of 0.25 ppm of O_3 for 4 to 6 hours. Lower doses stimulated spore germination in some cases.

7.6 EFFECTS OF OZONE OR TOTAL OXIDANTS ON SPECIFIC FOREST ECOSYSTEMS

In previous sections of this chapter, the effects of ozone or total oxidants on a variety of ecosystem components and on the interactions of respective components have been discussed. In this section, results are presented from extensive studies of the forest ecosystems of the San Bernardino Mountains in California, in which multiple species and trophic levels were examined, and from studies of the forest ecosystems of the Blue Ridge Mountains of Virginia.

7.6.1 The San Bernardino Mixed-Conifer Forest

One of the most thoroughly studied ecosystems in the United States is the mixed coniferous forest ecosystem in the San Bernardino Mountains of southern California. The San Bernardino Forest is located at the eastern end of the 80-mile-long South Coast Air Basin, where a severe air pollution problem has been created by the last three decades of extensive urban and industrial development (Miller and Elderman, 1977).

Ponderosa pine (*Pinus ponderosa* Laws) is one of five major species in this mixed-conifer forest, which covers wide areas of the western Sierra Nevada Mountains and other mountain ranges from 1000 to 2000 m (3000 to 6000 ft) in elevation, including the San Bernardino Mountains in southern California. Five forest subtypes exist (Miller and Elderman, 1977): (1) ponderosa pine, (2) ponderosa pine-white fir, (3) ponderosa pine-Jeffrey pine, (4) Jeffrey pine-white fir, and (5) Jeffrey pine. Above 2000 m, Jeffrey pine (*Pinus jeffreyi* Grev and Balf) replaces ponderosa pine. Other species in the forest are sugar pine (*Pinus lambertiana* Dougl.), white fir (*Abies concolor* Lindl.), incense cedar (*Libocedrus decurrens* Torr.), and California black oak (*Quercus kelloggii* Newb.).

Sensitive plant species in the San Bernardino National Forest, such as ponderosa pine, began showing unmistakable injury in the early 1950s (Miller and Elderman, 1977), but the source of the injury was not identified as ozone until 1962 (Miller et al., 1963). In some of the earliest studies of the San Bernardino forest, Parmeter et al. (1962) estimated that 25,000 acres of the mixed-conifer forest had been affected by photochemical oxidants, with ponderosa pines severely injured but with no injury at that time to associated species (Miller and Millecan, 1971). Subsequently, ground and aerial surveys showed that ponderosa and Jeffrey pines on 100,000 of 160,000 acres of the forest showed moderate to severe injury (Wert, 1969). Even in these early studies, Stark et al. (1968) reported that the oxidant-injured trees were more susceptible than healthy trees to infestation by bark beetles.

In 1968, an inventory was begun of a 575-acre study block where much injury was evident to establish, by means of a scoring system, the extent of injury of ponderosa pine trees $\geq$4 inches in diameter at breast height (dbh). A monitoring station was also established in 1968 to measure concentrations of total oxidants in the Rim Forest-Sky Forest area (elevation about 5500 ft), where total oxidants were then measured continuously for a minimum of 5 months per year from 1968 through 1972 (Mast Meter calibrated against buffered 2 percent potasium iodide; see Chapter 4 for details of the method). Monitoring during that period showed ozone concentrations $\geq$0.08 ppm for $\geq$1300 hours, with concentrations rarely decreasing below 0.05 ppm at night near the crest of the mountain slope (Miller, 1973). The 1-month averages of the daily maxima of total oxidant concentrations are given in Figure 7-2 by month for the 5 years of the study period (Miller, 1973). The data in Figure 7-2 also show the number of hours per month when the California oxidant standard of 0.1 ppm was exceeded. The most severe, single, daily maximum oxidant concentration in the area, 0.58 ppm, occurred in June 1970, between 4:00 and 9:00 p.m. PST (Miller, 1973).

It should be noted here that the San Bernardino Mountains, situated east of the Los Angeles basin, are often subjected to episodic or sustained high concentrations of ozone, partly because of the frequent occurrence there of "trapping inversions," that is, persistent elevated inversions. Precursors emitted into an inversion layer or into the layer below the base of an elevated inversion can produce relatively high ozone concentrations that persist for a considerable time period or over a considerable distance of wind travel from

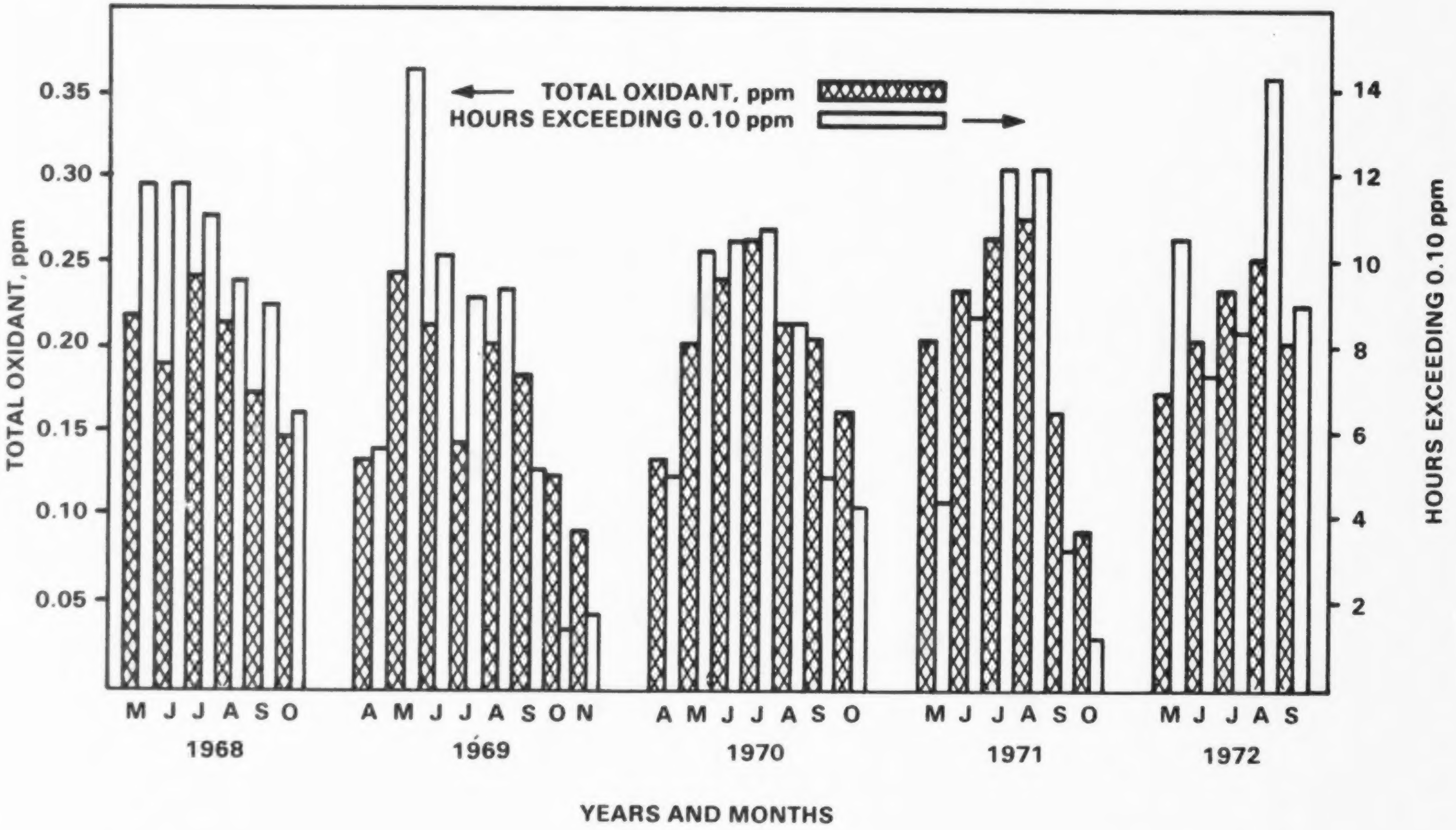

Figure 7-2. Total oxidant concentrations at Rim Forest (5640 ft.) in southern California during May through September, 1968 through 1972. Values of total oxidant are averages of daily maxima for a month. The number of hours in which total oxidant exceeded 0.10 ppm was also recorded for the 5 years.

Source: Miller (1973).

the precursor source area (Section 3.4.1). In addition, an increasing concentration gradient with increasing elevation occurs in the San Bernardino Mountains as the result of well-documented upslope flows (Section 5.5.2.4).

Based on the results of the inventory and of accompanying studies, some preliminary conclusions were drawn:

1. Ponderosa and Jeffrey pine were suffering the most injury. Mortality of one population of ponderosa pine (n = 160) was 8 percent between 1969 and 1971 ($p = 0.01$); in a second population (n = 40), mortality was 10 percent between 1968 and 1972. White fir populations had suffered slight damage, with scattered individual trees showing severe symptoms. Sugar pine, incense cedar, and black oak exhibited only slight foliar injury from oxidant exposure.
2. A substantial shift occurred in ponderosa pines from the "slight injury" category in 1969 to the "moderate injury" category in 1971, indicating that there was continuing oxidant stress and that the selective death of ponderosa pines was occurring.
3. Suppression of photosynthesis in seedlings was observed (Miller et al., 1969). In ponderosa pine saplings, needles shortened by exposure to oxidants returned to normal length when the seedlings were moved to ozone-free air during 1968 to 1973 (Miller and Elderman, 1977).
4. Bark beetles were judged to be responsible for the death of weakened trees in the majority of cases. Elimination of ponderosa pine from the mixed-conifer forest was postulated to occur in the future if the rate of bark beetle attack were to continue unabated (Cobb and Stark, 1970).
5. Aerial portions of ozone-injured pine trees showed a decrease in vigor that was associated with deterioration of the feeder root system (Parmeter et al., 1969).
6. Seed production was decreased in injured pines. Ordinarily, trees 25 to 50 inches dbh produce the most cones, but they were also the most sensitive to oxidants (Luck, 1980).
7. Understory plant species sensitive to oxidant pollution may already have been removed by air pollution stress at the time of these early studies (Miller and Elderman, 1977).

Because earlier studies of the effects of oxidants on the mixed-conifer forest left many questions unanswered, a comprehensive interdisciplinary study involving scientists at the University of California at Berkeley and Riverside and at the U.S. Forest Service Pacific Southwest Experiment Station (and financed by the U.S. Environmental Protection Agency) was begun in 1973 and terminated in 1978. This study is the most comprehensive and best-documented report on the effects of oxidants on a forest ecosystem (Miller et al., 1982).

The study was designed to answer two questions (Miller et al., 1982): (1) How do the organisms and biological processes of the conifer forest respond to different levels of chronic oxidant exposure; and (2) how can these responses be interpreted within an ecosystem context?

The major abiotic components studied were water (precipitation), temperature, light, mineral nutrients (soil substrate), and oxidant pollution. The biotic components studied included producers (an assortment of tree species and lichens), consumers (wildlife, insects, disease organisms), and decomposers. The decomposers studied were the populations of saprophytic fungi responsible for the decay of leaf and woody litter.

The research plan included study of limited aspects of the following ecosystem processes: (1) carbon flow (the movement of carbon dioxide into the plant, its incorporation into carbohydrates; and then its partitioning among consumers, decomposers, litter, and the soil; and finally its return to the atmosphere); (2) the movement of water in the soil-plant-atmosphere continuum; (3) mineral nutrient flow through the green plant, litter, and soil-water compartments; and (4) the shift in diversity patterns in time and space as represented by changes in age, structure, and density in the composition of tree species in communities.

In addition to the Rim Forest-Sky Forest station established in 1968, six other monitoring stations were established along the mountain crests near the vegetational study sites in order to characterize the east-to-west oxidant gradient. Hourly average O_3 concentrations for 1975 (measured by UV) indicated that O_3 buildup began around 10 a.m. and reached a maximum at all stations in all months (May through September) at around 4 p.m. For example, at the Rim Forest-Sky Forest Station where the highest concentrations were usually recorded, the 1-month average of hourly values for May through September 1975 ranged from 0.07 to 0.10 ppm at 10 a.m. and from 0.15 to 0.22 ppm at 4 p.m. The highest concentrations occurred in June, July, and August, and the lowest for the 5-month period occurred in September. The total number of hours with concentrations of 0.08 ppm or more during June through September was never less than 1300 hours per season during the first 7 years (1968 through 1974) (Miller and Elderman, 1977).

From 1973 through 1978, 24-hour ozone concentrations ranged from a background of 0.03 to 0.04 ppm in the eastern part of the San Bernardino Mountains to maxima of 0.10 to 0.12 ppm in the western part (Miller et al., 1982). Monthly averages of daily maxima of oxidant concentrations for 1968 through 1972 were given in Figure 7-2. Annual trends of O_3, precipitation, and temperature as measured May through September, 1972 through 1978, are shown in Figure 7-3 (Miller et al., 1982). In addition to total oxidant, PAN and NO_2 concentrations were measured at the Sky Forest station. Symptoms of PAN injury were not distinguishable from O_3 on herb-layer plant species, while NO_2 remained at non-toxic concentrations.

The interdisciplinary studies indicated that the ecosystem components most directly affected by O_3 were the tree species, the fungal microflora of tree needles, and foliose lichens growing on the bark of trees. Injury to or changes in the functioning of the living components also affected, either directly or indirectly, the ecosystem processes of carbon flow, mineral nutrient cycling, and water movement; and also changed vegetational community patterns (Miller et al., 1982).

Ponderosa pine was the most sensitive of the trees to O_3, with Jeffrey pine, white fir, black oak, incense cedar, and sugar pine following in decreasing order of sensitivity. Foliar injury on sensitive ponderosa and Jeffrey pine was observed when the 24-hour-average ozone concentrations were 0.05 to 0.06 ppm (Miller et al., 1982). Injury, decline, and death of these species suggested a chain of events that could lead to various levels of ecosystem changes, depending on the ozone concentrations (Miller et al., 1982). Foliar injury, premature senescence, and needle fall decreased the photosynthetic capacity of stressed pines and reduced the production of carbohydrates needed for use in growth and reproduction by the trees. Nutrient availability to the trees was also reduced by their retention of smaller amounts of green foliage (Miller et al., 1982). Decreased carbohydrate resulted in a decrease in radial growth and in height of stressed trees (McBride et al., 1975; Miller and Elderman, 1977). Growth reductions attributable to oxidant air pollution were calculated by McBride et al. (1975) for ponderosa pine saplings. Assuming 1910 to 1940 to be a period of low oxidant pollution and 1944 to 1974 a period of high oxidant pollution, they used radial growth increments (dbh) to calculate an oxidant-induced decrease in diameter of 40 percent. On the basis of the

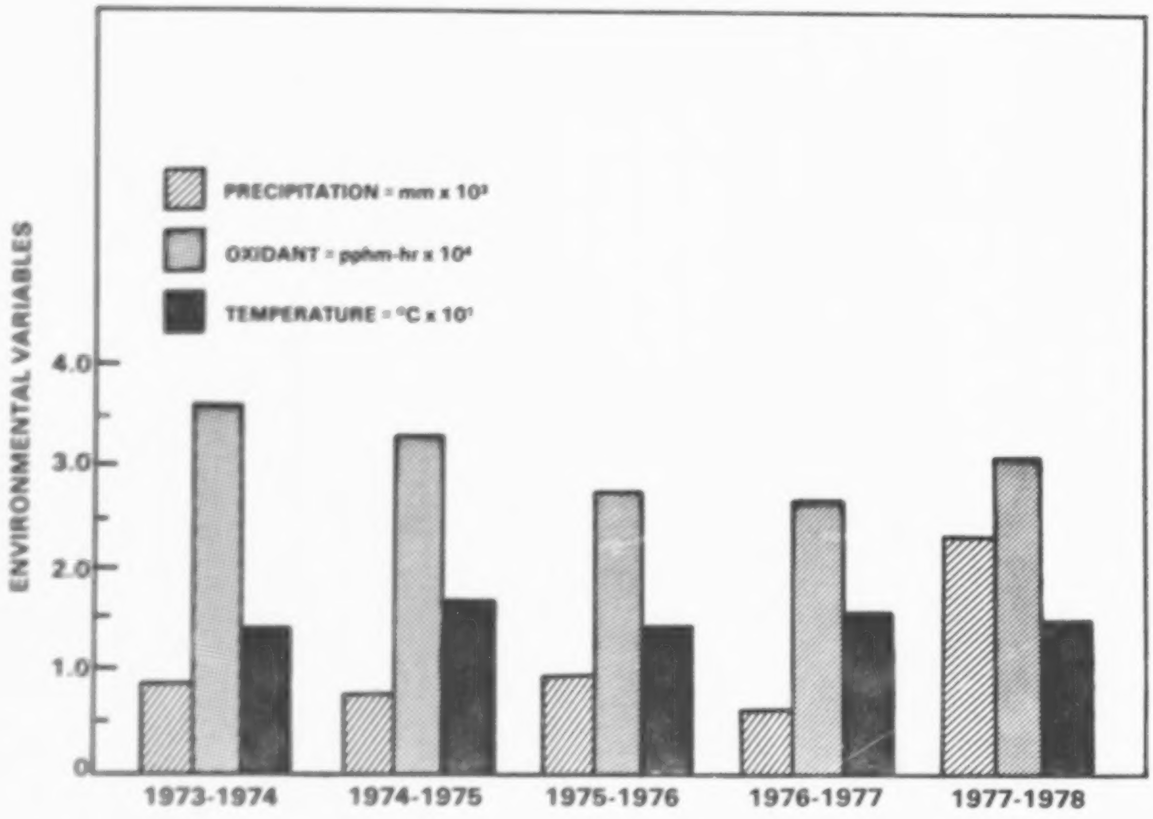

Figure 7-3. Annual trends of oxidant dose, precipitation, and air temperature near the Lake Arrowhead-Sky Forest region of the San Bernardino National Forest, California.

Source: Miller et al. (1982).

3-year growth of saplings in filtered and nonfiltered air in portable greenhouses, they calculated oxidant-induced reductions of 26 percent in height growth (McBride et al., 1975). As noted also for the radial growth studies cited in Section 7.4.1.2, standardized methods for measuring tree rings had not been developed at the time of this study. Consequently, calculated decreases in diameter would reflect uncertainties associated with radial growth measurements. Calculated decreases in growth in height were based on the assumption of a growth rate in non-stressed older trees equivalent to that in non-stressed saplings.

Tree reproduction also was influenced by a reduction in carbohydrate. Injured ponderosa and Jeffrey pines older than 130 years produced significantly fewer cones per tree than uninjured trees of the same age (Luck, 1980). Tree ring analysis showed declines of ring width indices for many trees. In recent years, however, stand thinning reversed the trend (Miller et al., 1982).

A comparison of lichen species found on conifers during the years 1976 to 1979 with collections from the early 1900's showed the presence of 50 percent fewer species in the more recent period. Marked morphological deterioration of the common species *Hypogymnia enteromorpha* was documented in areas of high oxidant concentrations (Sigal and Nash, 1983).

Biotic interactions associated with predators, pathogens, and symbionts were influenced by changes in the energy available to the trees. The decrease in vigor and lack of ability to recover from ozone injury associated with reduced carbohydrates made the ponderosa pines more susceptible to attack by predators and pathogens (Stark and Cobb, 1969). Dahlsten and Rowney (1980) have pointed out that oxidant-weakened pines can be killed by fewer western pine beetles than are required to kill healthier trees. In stands with a high proportion of O_3-injured trees, a given population of western pine beetles could therefore kill more trees. James et al. (1980a,b) observed that the root rot fungus, *H. annosum*, increased more rapidly because freshly cut stumps and roots of weakened trees were more vulnerable to attack.

Carbon flow and mineral nutrient cycling were also influenced by litter accumulation. Heavy litter accumulation occurred in stands with the most severe needle injury and defoliation. The heaviest accumulation was beneath trees with moderate damage rather than the most severe damage. Carbon and mineral nutrients accumulated in the thick needle layer and influenced nutrient availability because of potential losses by volatilization during fires and in subsequent surface runoff (Miller et al., 1982). Mineral nutrient cycling was also influenced by the change in microflora of pine needles and its relationship with the decomposer community. Premature senescence and abscission of pine needles alter the taxonomic diversity and population density of the microflora that normally develop on needles during the time they are growing on trees. The change in the types of fungi on needles and a decrease in their numbers weaken the decomposer community and the rate of decomposition (Bruhn, 1980).

Litter decomposition rate may also be influenced by decreases in moisture on the forest floor caused by a thinning of the canopy. A thinner canopy allows more sunlight to reach the forest floor and dry the litter more rapidly, thus potentially decreasing the rates of decomposition and of subsequent nutrient cycling, and increasing litter depth. Pine seedling establishment is expected to be hindered by deep litter but the establishment of oxidant-tolerant over- and understory species is expected to be favored.

Existing data are inadequate for explaining how the complex interplay of ozone injury, insects, diseases, and drought and, to an extent, fire, will shape the age and species structure, in the future, of the tree communities studied (Miller et al., 1982). It is more prudent to propose a range of possible changes in forest composition. In a worst-case example, the ozone-incited stress on sensitive ponderosa and Jeffrey pine and, to a lesser extent on sensitive white fir, black oak, incense cedar, and sugar pine, if accompanied by fire, would bring about the removal of the pine forest overstory. In the understory of ozone-weakened stands of ponderosa pine, the establishment of ozone-tolerant species, particularly incense cedar, forms a fuel ladder that threatens the survival of the overstory pines in the event of fire. At the chaparral-forest boundary, a shift in dominance to self-perpetuating, fire-adapted, ozone-tolerant shrub and oak species has occurred following thinning of the overstory pines and has produced species mixtures that provide fewer commodity and amenity values than the former forest (Miller et. al., 1982).

Many of the changes observed in the components, structure, and processes of the San Bernardino forest ecosystems, attributed by a number of investigators to ozone-oxidant stress, are consistent with the theories of Odum (1985) on trends expected to occur in stressed ecosystems. The changes postulated by Odum that have been observed in the San Bernardino mixed-conifer ecosystem include: (1) low efficiency in converting energy to organic structure;

(2) decreased nutrient cycling between trophic levels; (3) decreased nutrient availability (via retention in litter); (4) increased proportion of r-strategists (opportunistic species); (5) decreased size and decreased lifespans of organisms or parts (e.g., needles); (6) reversal of autogenic successional trends (succession reverts to earlier stages); and (7) decreased mutualism (positive interactions) and increased parasitism (negative interactions).

7.6.2 The Blue Ridge Mountains of Virginia

Oxidant-induced injury on vegetation has been observed in the Appalachian Mountains in the eastern United States for many years. Needle blight of eastern white pine was first reported in the early 1900s but it was not until 1963 that it was shown to be the result of acute and chronic O_3 exposure (Berry and Ripperton, 1963).

Despite early reports by Berry (1961, 1964) and by Berry and Ripperton (1963), no concerted effort to determine the effects of ozone on the vegetation of the Appalachian Mountains was made until Hayes and Skelly (1977) monitored total oxidants and recorded oxidant-associated injury on eastern white pine in three rural Virginia sites between April 1975 and March 1976. Injury was associated with total oxidant peaks of 0.08 ppm or higher.

Increased injury symptoms were observed by Hayes and Skelly (1977) on pine trees previously categorized as sensitive or intermediately sensitive following O_3 exposures. No injury was observed on trees categorized as tolerant. Hayes and Skelly (1977) suggested that continued exposure of sensitive and intermediately sensitive white pine to acute and chronic oxidant concentrations could ultimately influence their vegetative vigor and reproductive ability. Inability to reproduce could result in replacement of the sensitive pines by tolerant species.

More recent studies have reported oxidant-induced symptoms on other indigenous forest tree species: tulip poplar, green ash (*Fraxinus pennsylvanica*, Marsh), hickory (*Carya* spp.), black locust (*Robinia pseudoacacia* L.) hemlock (*Tsuga canadensis* (L.) Carr.), and table mountain (*Pinus pungens*, Lamb), Virginia (P. *virginiana*, Mill.), and pitch pine (P. *rigida*, Mill.) (Duchelle et al., 1982). Monthly 8-hour average O_3 concentrations ranged from 0.035 to 0.065 ppm and peak hourly concentrations from 0.08 to 0.13 ppm (Skelly et al., 1984) (Table 7-4). Sulfur dioxide concentrations ranged from undetectable to 0.03 ppm.

TABLE 7-4. MONTHLY 8-hr AVERAGE (11:00 a.m. - 6:00 p.m. EST), MONTHLY AVERAGE OF PEAK 1-hr, AND CUMULATIVE SEASONAL OZONE DOSES MONITORED AT BIG MEADOWS, SHENANDOAH NATIONAL PARK, VIRGINIA, DURING 1979-1981 (ppm)

Month	YEAR					
	1979		1980		1981	
	Average	Peak	Average	Peak	Average	Peak
January	0.041	0.06	0.020	0.03	0.033	0.06
February	-[a]	-	0.024	0.04	0.030	0.06
March	0.062	0.10	0.035	0.04	0.028	0.05
April	0.055	0.10	0.042	0.07	0.043	0.07
May	0.052	0.08	0.048	0.10	0.037	0.08
June	0.055	0.08	0.059	0.09	0.023	0.06
July	0.047	0.09	0.058	0.09	0.037	0.10
August	0.054	0.07	0.051	0.10	0.030	0.06
September	0.046	0.09	0.046	0.09	0.037	0.06
October	0.042	0.08	0.033	0.08	0.044	0.09
November	0.039	0.07	0.035	0.06	0.055	0.08
December	0.028	0.05	0.041	0.06	-	-
Total ozone dosage 1 April-30 September, ppm-hr	73.38		74.22		50.51	

[a] Data not available.

Source: Duchelle et. al. (1983).

Injury to herbaceous vegetation growing in the same areas was also observed (Duchelle et al., 1983). Ambient O_3 concentrations were shown to reduce growth and productivity of graminoid and forb vegetation in the Shenandoah National Park. For each year of the study, biomass production (weight of living tissue) was greatest in filtered-air open-top chambers. The total 3-year cumulative dry weight of the plants in the filtered chambers was significantly (<0.05) greater than that of plants in non-filtered and open-air plots. Similar cumulative O_3 doses in 1979 and 1980 resulted in different percentage reductions in biomass for the two years, suggesting that variations in O_3 dose during the growing season may be more important than the cumulative O_3 dose. Ozone inhibits biomass production of natural vegetation. Reductions in biomass could be a consequence of decreased root growth resulting from O_3 exposure. Common milkweed (*Ascelepias syrica* L.) and common blackberry (*Rubus allegheniensis* Porter) were the only two native species to develop visible injury. Milkweed has previously been shown to be very sensitive to O_3 (Duchelle and Skelly, 1981).

Ozone episodes lasting 1 to 3 days occurred several times each year during the period of the study. Peak hourly concentrations, measured from 11:00 a.m. through 6:00 p.m., ranged from 0.08 to 0.10 ppm; however, daytime ozone concentrations exceeding 0.06 ppm were recorded for 1218, 790, and 390 hours during 1979, 1980, and 1981, respectively. As noted in Section 7.1.4.2, however, measurements of only daytime ozone concentrations may not capture the true ozone maxima in areas affected by transport, or unique meteorological conditions, or both. Concentrations of SO_2 ranged from <0.001 to 0.03 ppm and were considered to have had no effects on vegetation (Duchelle et al., 1983).

As in California, ozone is transported to these sites from distant urban and industrial sources. In the Blue Ridge and Appalachian Mountains, these sources include the industrial midwest, eastern Virginia, and the Washington, DC, area. Most of the episodes monitored were regional in nature. High O_3 concentrations occurred at the three monitoring sites simultaneously (Table 7-3, Skelly et al., 1984).

The effects of ozone on species composition and succession of natural vegetation of the Virginia mountains were not studied; however, none of the plant species shown to be injured by ozone plays a dominant role in the Blue Ridge Mountain ecosystem. Therefore, the removal of any of these species would probably not have the impact that the decline and death of ponderosa and Jeffrey pine have had on the San Bernardino Forest ecosystem.

7.7 RESPONSES OF OTHER ECOSYSTEMS TO OZONE

7.7.1 Responses of Native Vegetation

No other natural ecosystem has been as thoroughly studied as the San Bernardino National Forest. However, the same patterns of response to ozone stress seen there have been observed in other locations (Section 7.3). Sensitive individuals of various species were adversely affected by O_3. Photosynthesis was inhibited and reductions occurred in carbohydrate formation and translocation, in biomass production, in growth, and in reproductive capacity. The larger or dominant species were those most severely affected. Changes in community structure were predicted for some of the vegetational communities on the basis of observed effects.

California

In southern California, the predominant native shrubland vegetation consists of chaparral and coastal sage scrub. Chaparral occupies upper elevations of the coastal mountains and extends into the North Coast ranges, east to central Arizona, and south to Baja California. Coastal sage scrub occupies lower elevations of the coastal and interior slopes of ranges extending from San Francisco to Baja California. Applying standard plant ordination techniques, Westman (1979) found reduced cover of native species of coastal sage scrub on some sites. The reduced cover was statistically correlated with elevated levels of atmospheric oxidants. From the data records of nearby monitoring stations, an annual average concentration of 0.18 ppm was calculated for the 11 most polluted sites; the annual average concentration calculated for the 11 least-polluted sites was 0.04 ppm. The effect of long-term, continued injury was to decrease foliar cover of vegetation and species richness by favoring a few, tolerant species.

Stolte (1982) also studied chaparral species and their response to ozone under both experimental and ambient air conditions. A large variation in sensitivity to O_3 from species to species of seedling chaparral plants was observed; however, the majority appeared to be intermediate in sensitivity. Ozone-sensitive chaparral seedlings can have reduced vigor and suffer higher mortality. Stolte (1982) found that the composition and density of chaparral stands are determined by seedling success of the dominant species and that these species in turn influence the behavior of the stands during fires. Composition and density of chaparral stands may be permanently altered, since the post-fire seedling establishment of perennial dominants occurs chiefly during the first year following fire.

Utah

Treshow and Stewart (1973) conducted one of the few studies concerned with the impact of air pollution on native herbaceous species in natural plant communities. The aim of the study was to determine the concentration of ozone necessary to cause foliar injury to the most prevalent species in some of the intermountain grassland, oak, aspen, and conifer communities. Seventy common plant species indigenous to those communities were fumigated with ozone to establish sensitivity. Injury was generally evident at concentrations above 0.15 ppm for 2 hours. Species found to be most sensitive to ozone in the grassland and aspen communities included some dominant species considered key to community integrity. *Bromus tectorum* L. (cheatgrass), the most prevalent species in the grassland community, was also the most sensitive. Severe injury to this introduced annual resulted from a single 2-hour exposure to 0.15 ppm of ozone. Cheatgrass is widely distributed in the intermountain western United States. Removal of this dominant species from plant communities could result in a shift in dominance to another species. The significance of such a change would depend on the species replacing cheatgrass. The other grasses studied were not as sensitive to ozone, nor were the forbs (Table 7-5). The production of carbohydrates in visibly injured grasses, however, was significantly reduced.

In the aspen community, the most dramatic example was aspen (*Populus tremuloides* Michx.) itself. A single 2-hour exposure to 0.15 ppm ozone caused severe symptoms on 30 percent of the foliage. Because white fir seedlings require aspen shade for optimal juvenile growth, the authors suggested that significant losses in aspen populations might restrict white fir development and later forest succession; conversion to grasslands could occur. It was apparent that in a natural community exposed to ozone, the tolerant species would soon become the dominants. The authors concluded that ozone must be considered a significant environmental parameter that influences the composition, diversity, and stability of natural plant communities and that it "may ultimately play a major role in plant succession and dominance" (Treshow and Stewart, 1973).

National Parks and National Recreation Areas

Vegetation in national parks other than the Shenandoah National Park is apparently also being injured by ambient air pollutants. In a recent report to Congress, the National Park Service (1985) stated that the preliminary results of studies recently completed or currently under way in a number of parks indicate that sensitive vegetation is being injured by O_3 transported into the parks. Vegetational injury from O_3 has been observed in the Santa Monica Mountains National Recreation Area; Sequoia, Kings Canyon, Shenandoah, Great Smoky Mountains, and Acadia National Parks; Indiana Dunes National Lakeshore; and Congaree Swamp National Monument Park. Maximum hourly average ozone concentrations ranged from 0.11 ppm in the Great Smoky Mountains National Park to 0.22 ppm in the Santa Monica Mountains. Sulfur dioxide concentrations

TABLE 7-5. INJURY THRESHOLDS FOR 2-hr EXPOSURES TO OZONE

Species	Injury threshold, ppm O_3 for 2 hr
Grassland-oak community species:	
Trees and shrubs:	
Acer grandidentatum Nutt.	>0.40
Acer negundo L.	>0.25
Artemesia tridentata Nutt.	0.40
Mahonia repens G. Don	>0.40
Potentilla fruticosa L.	0.30
Quercus gambelii Nutt.	0.25
Toxicodendron radicans (L.) Kuntze	>0.30
Perennial forbs:	
Achillea millefolium L.	>0.30
Ambrosia psilostachya DC.	>0.40
Calochortus nuttallii Torr.	>0.40
Cirsium arvense (L.) Scop.	0.40
Conium maculatum L.	>0.25
Hedysarum boreale Nutt.	0.15
Helianthus anuus L.	>0.30
Medocago sativa L.	0.25
Rumex crispus L.	0.25
Urtica gracilis Ait.	0.30
Vicia americana Muhl.	>0.40
Grasses:	
Bromus brizaeformis Fisch & Mey.	0.30
Bromus tectorum L.	0.15
Poa pratensis L.	0.25
Aspen and conifer community species:	
Trees and shrubs:	
Abies concolor (Gord. & Glend.) Lindl.	0.25
Amelanchier alnifolia Nutt.	0.20
Pachystima myrsinites (Pursh) Raf.	>0.30
Populus tremuloides Michx.	0.15
Ribes hudsonianum Richards	0.30
Rosa woodsii Lindl.	>0.30
Sambucus melanocarpa A. Gray	>0.25
Symphoricarpos vaccinioides Rydb.	0.30
Perennial forbs:	
Actaea arguta Nutt.	0.25
Agastache urticifolia (Benth.) Kuntz	0.20
Perennial forbs:	
Allium acuminatum Hook	0.25
Angelica pinnata S. Wats.	<0.25
Aster engelmanni (Eat.) A. Gray	0.15
Carex siccata Dewey	0.30
Cichorium intybus L.	0.25
Cirsium arvense (L.) Scop.	<0.40
Epilobium angustifolium L.	0.30
Epilobium watsoni Barbey	0.30
Erigonum heraclioides Nutt.	0.30
Fragaria ovalis (Lehm.) Rydb.	0.30
Gentiana amarella L.	>0.15
Geranium fremontii Torr.	<0.25
Geranium richardsonii Fisch. & raut.	0.15
Juncus sp.	>0.25
Lathyrus lanzwertii Kell.	>0.25
Lathyrus pauciflorus Fern.	0.25
Mertensia arizonica Greene	0.30
Mimulus guttatus DC.	>0.25
Mimulus moschatus Dougl.	<0.40
Mitella stenopetala Piper	>0.30
Osmorhiza occidentalis Torr.	0.25
Phacelia heterophylla Pursh	<0.25
Polemonium foliosissimum A. Gray	0.30
Rudbeckia occidentalis Nutt.	0.30
Saxifraga arguta D. Don	<0.30
Senecio serra Hook.	0.15
Taraxacum officinale Wiggers	>0.25
Thalictrum fendleri Engelm.	>0.25
Veronica anagallis-aquatica L.	0.25
Vicia americana Muhl.	>0.25
Viola adunca Sm.	>0.30
Annual forbs:	
Chenopodium fremontii Wats.	<0.25
Collomia linearis Nutt.	<0.25
Descurainia californica (Gray) O.E. Shulz	0.25
Galium bifolium Wats.	>0.30
Gayophytum racemosum T. & G.	0.30
Polygonum douglasii Greene	>0.25
Grasses:	
Agropyron caninum (L.) Beauv.	>0.25
Bromus carinatus Hook. & Arn.	<0.25

Source: Treshow and Stewart (1973).

were below limits of detection in most of the parks, but were 0.01 ppm (maximum 3-hr) in the Shenandoah National Park and 0.25 ppm (maximum 3-hr) in the Indiana Dunes National Lakeshore. The impact of the injured vegetation on these ecosystems has yet to be appraised.

7.7.2 Managed Forest Ecosystems

Agricultural ecosystems are managed ecosystems that are manipulated to maximize their yields for the benefit of humans. While their importance cannot be overemphasized, agricultural ecosystems are not the only managed ecosystems of importance in the United States.

The largest ecosystems managed for human use are the forests in the National Forest System under the U.S. Department of Agriculture. They encompass 190 million acres, primarily in the west. The National Forest System provides nearly one-fourth of the softwood timber used in the United States. Commercial timber production is only one use of U.S. forestlands. Wildlife habitat, rangeland, watershed protection, wilderness, and recreation are other uses. These forests, if exposed to ozone, are potentially susceptible to the same ozone-induced effects observed in the forest ecosystems of the San Bernardino and Blue Ridge Mountains.

7.7.3 Aquatic Ecosystems

Terrestrial and aquatic ecosystems are closely interrelated. An adverse impact on a forest ecosystem may in turn adversely affect adjacent aquatic systems. A variety of linkages for energy and nutrient exchange exist. Air pollution stress on terrestrial ecosystems often triggers dysfunctions, e.g., disruption of life cycles of aquatic insects, in neighboring aquatic ecosystems such as streams, lakes, and reservoirs. Sediments resulting from erosion can change the physical character of stream channels, causing changes in bottom deposits, erosion of channel banks, obstruction of flow, and increased flooding. They can fill in natural ponds and reservoirs. Finer sediments can reduce water quality, affecting public and industrial water supplies and recreational areas. For example, Westman (1977) has estimated that oxidant damage in the San Bernardino Forest area could result in a cost of $27 million per year (1973 dollars) for sediment removal, as long as the early successional stages lasted, assuming sediment runoff to be equally partitioned among streets, sewers, and debris basins. This estimate, however, was based on the assumption that forest fires would virtually devastate any oxidant-weakened stands, resulting in almost total removal of vegetation.

Turbidity caused by increased erosion can also reduce the penetration of light into natural waters. This, in turn, can reduce aquatic plant photosynthesis and can lower the supplies of dissolved oxygen, leading to changes in the natural flora and fauna (Bormann and Smith, 1980). Significant forest alterations, therefore, may have a regional impact on nutrient cycling, soil stabilization, sedimentation, and eutrophication of adjacent or nearby aquatic systems. Interfacing areas, such as wetlands and bogs, may be especially vulnerable to impact.

As noted in the San Bernardino studies, forest biomass reduction results in a corresponding reduction in the total inventory of nutrient elements held within a system. Loss of the dominant vegetation disrupts cycling pathways and mechanisms of nutrient conservation. Research on the northern hardwood forest has clearly established that retention of nutrients within a forest ecosystem depends on constant and efficient cycling between the various components of the intrasystem cycle and that deforestation impairs this retention (Likens et al., 1977). Extensive nutrient loss can pollute downstream aquatic resources, resulting in enrichment or eutrophication of a site, with long-term consequences for potential plant growth, as well as contamination of urban water sources.

7.8 ECONOMIC VALUATION OF ECOSYSTEMS

According to economic theory, the price of goods or services in the marketplace represents the value that society places on those goods and services. Free goods and services are often viewed in the marketplace as valueless or simply as existing outside of the economy. Natural ecosystems provide free public and private goods and services, but at present no agreement exists as to the value of an ecosystem to society and the inherent values of natural ecosystems have not been incorporated into any valuation system (Farnworth et al., 1981).

The price of goods and services in the marketplace has some correspondence, however minimal in some instances, to the cost of producing and offering those goods and services in the marketplace. In the case of natural ecosystems, however, human investment of energy and resources is quite low. Whereas agricultural ecosystems (as well as animal husbandry) require intensive management and dollar expenditures for the production of marketable food items, natural ecosystems commonly provide societal benefits (including some edible foodstuffs) without the investment of appreciable direct dollar expenditures or intensive management.

In an attempt to provide a framework for valuing ecosystems, Farnworth et al. (1981) separated "value" into (1) market values of private goods (Value I) and (2) non-market values of public goods and services. In turn, they separated non-market values into attributable or assignable values (Value II) and intangible or non-assignable values (Value III). According to Farnworth et al. (1981), political mechanisms, as opposed to the marketplace, are used to assign a price or value to Value II items because society believes that the value assigned by the marketplace is inadequate. Value III items are not viewed by Farnworth et al. (1981) as having been incorporated into either marketplace economics or political mechanisms. It might be noted here, however, that the United States has indirectly placed a price or value on certain Value II and III items, such as ecosystems, by allocating resources for the abatement of air pollution thought to have potentially deleterious effects on such items. Nevertheless, the apportionment of the costs (price or value) of abating air pollution to the respective Value II and III items (as well as many Value I items) remains unresolved.

Natural ecosystems, such as forests maintained as wilderness areas, may offer products and services of little direct dollar value, but they provide critically important, if unpriced, benefits to society. These benefits include, but are not restricted to: (1) maintenance of the global carbon balance and the O_2-CO_2 cycle; (2) soil stabilization (flood and erosion control); (3) enhanced air and water quality; (4) nutrient conservation; (5) energy conservation; (6) gene preservation; and (7) amenity and aesthetic functions, ranging from tourism and birdwatching to white-water rafting and hunting (Smith, 1970; Bormann, 1976; Westman, 1977; National Research Council, 1977; Hutchinson et al., 1982).

Such goods and services, ranging from the critically essential to the "nice but not necessary," are extremely difficult to quantify or to monetize once quantified. Additional knowledge is needed in several important areas before credible valuations of ecosystems can be made. First, better and more complete information is needed on all the functions performed by ecosystems

(Farnworth et al., 1981). Second, a framework must be constructed for converting benefits from or losses of goods and services from ecosystems to a value system that permits comprehension of the true value of ecosystems. The costs to society of stresses on ecosystems from ozone or any other manmade influence will not be known and will almost certainly be underestimated unless such an accounting system is developed (Risser, 1985). Third, additional and better information is needed on the amount of chronic stress (e.g., ozone-oxidant pollution) natural ecosystems can sustain and still retain ecosystem integrity; on how long can they sustain stress and remain resilient, having the capacity for self-repair; and on how much time is required for return to their original state once such chronic stresses have been reduced or eliminated (see, e.g., West et al., 1980; cited in Taylor and Norby, 1985). At present, knowledge is lacking on whether oxidant-stressed ecosystems are being damaged irreversibly.

The above information, at a minimum, is needed for the credible economic valuation of natural ecosystems. Still further information is needed to permit credible economic valuations of ozone-induced damage to ecosystems. While areas requiring additional data are clear from a reading of this chapter, the following two areas are especially obvious:

1. Better aerometric data for ecosystems suspected of being under stress from ozone;

2. Measurement of additional variables in order to rule out significant contributions to observed effects by temperature and other climatic conditions, other airborne or water-borne pollutants, and biotic agents (pathogens and other pests), as well as interactions among and between biotic and non-pollutant abiotic factors (see, e.g., Manion, 1985; Cowling, 1985; Prinz, 1985; Smith, 1985, McLaughlin, 1985; Taylor and Norby, 1985).

7.9 SUMMARY

7.9.1 Responses of Ecosystems to Ozone Stress

The responses to ozone of individual species and subspecies of herbaceous and woody vegetation are well documented. They include (1) injury to foliage, (2) reductions in growth, (3) losses in yield, (4) alterations in reproductive capacity, and (5) alterations in susceptibility to pests and pathogens, especially "stress pathogens" (National Research Council, 1977; U.S. Environmental Protection Agency, 1978; this document, Chapter 6). The responses elicited by ozone in individual species and subspecies of primary producers (green plants) have potential consequences for natural ecosystems because effects that alter the interdependence and interrelationships among individual components of populations can, if the changes are severe enough, perturb ecosystems. Because, however, of the numerous biotic and abiotic factors known to influence the response of ecosystem components such as trees (see, e.g., Cowling, 1985; Manion, 1985), it is difficult to relate natural ecosystem changes to ozone specifically, and especially to ozone alone. Ozone can only be considered a contributing factor.

Evidence indicates that any impact of ozone on ecosystems will depend on the responses to ozone of the producer community. Producer species (trees and other green plants) are of particular importance in maintaining the integrity of an ecosystem, since producers are the source, via photosynthesis, of all new organic matter (energy/food) added to an ecosystem. Any significant alterations in producers, whether induced by ozone or other stresses, can potentially affect the consumer and decomposer populations of the ecosystem, and can set the stage for changes in community structure by influencing the nature and direction of successional changes (Woodwell, 1970; Bormann, 1985), with possibly irreversible consequences (see, e.g., Odum, 1985; Bormann, 1985).

7.9.2 Effects of Ozone on Producers

In forest ecosystems, tree populations are the producers. As such, they determine the species composition, trophic relationships, and energy flow and nutrient cycling of forest ecosystems (Ehrlich and Mooney, 1983). Ozone-induced effects on the growth of trees has been clearly demonstrated in controlled studies (see Chapter 6). For example, Kress and Skelly (1982) showed the following reductions in growth in height in seedlings exposed to ozone for 6 hr/day for 28 days: American sycamore, 9 percent (0.05 ppm O_3); sweetgum, 29 percent (0.10 ppm O_3); green ash, 24 percent (0.10 ppm); willow oak, 19 percent (0.15 ppm O_3); and sugar maple, 25 percent (0.15 ppm). Similar results have been obtained for other tree species by other investigators (e.g., Dochinger and Townsend, 1979; Mooi, 1980; Patton, 1981; Kress et al., 1982). Some species, however, have been shown to exhibit increased growth in short-term ozone exposures (e.g., yellow poplar and white ash; Kress and Skelly, 1982). Hogsett et al. (1985) found reductions in growth in height, in radial growth, and in root growth in slash pine seedlings exposed for up to

112 days to 7-hr seasonal mean concentrations of 0.104 ppm O_3 (with a 1-hr daily maximum of 0.126 ppm O_3) and 0.076 ppm O_3 (with a 1-hr daily maximum of 0.094 ppm O_3).

Field studies on the Cumberland Plateau (near Oak Ridge, TN) have shown reductions in growth in eastern white pine exposed to ambient air O_3 concentrations $\geq$0.08 ppm (1-hr) (Mann et al., 1980), with 1-hr concentrations ranging over the multi-year study from 0.12 ppm to 0.2 ppm (McLaughlin et al., 1982). It should be noted, however, that in the McLaughlin et al. (1982) study trees classified as ozone-tolerant sustained greater percentage reductions in radial growth in the last 4 years (1976 to 1979) of the 1962 to 1979 period for which growth was examined than the reductions observed in trees classified as ozone-sensitive. In the Blue Ridge Mountains of Virginia, Benoit et al. (1982) found reductions in radial growth of sensitive eastern white pine in a multi-year study in which 1-hr O_3 concentrations were generally 0.05 to 0.07 ppm but peaked at $\geq$0.12 ppm on as many as 5 consecutive days at a time.

The concentrations of ozone reported for sites on the Cumberland Plateau and in the Blue Ridge Mountains may not fully represent the actual exposures at those sites, however, since measurements were made in the daytime only. For species in which stomates remain open at night, such as eastern white pine, the possible occurrence of peak ozone concentrations at night, from transported urban plumes, is an important consideration for accurately assessing concentration-response relationships.

Exposures of trees and other producers to ozone have been shown to reduce photosynthesis (e.g., Miller et al., 1969; Botkin et al., 1972; Barnes, 1972; Carlson, 1979; Coyne and Bingham, 1981; Yang et al., 1983; Reich and Amundson, 1985) and to alter carbohydrate allocation, especially the partitioning of photosynthate between roots and tops (e.g., Price and Treshow, 1972; Tingey et al., 1976; McLaughlin et al., 1982). Krause et al. (1984) have associated growth reductions in ozone-exposed seedlings with foliar leaching. All three of these effects have been postulated as mechanisms of the reduced growth seen in ozone-exposed vegetation.

Responses to ozone are not uniform among plants of the same species and the same approximate age. Differential responses have been attributed in part to differences in genetic potential (e.g., Mann et al., 1980; Coyne and Bingham, 1981; Benoit et al., 1982). In addition, the age of the plant and its developmental stage at time of exposure influence its response to ozone (see Chapter 6).

Other factors, as well, influence the types and magnitude of plant responses to ozone, including such macro- and microenvironmental factors as temperature, relative humidity, soil moisture, light intensity, and soil fertility (see Chapter 6).

Trees may respond rapidly to O_3 stress. Needles of sensitive eastern white pine usually exhibit injury symptoms within a few days after exposure to high O_3 concentrations. In other instances, responses are more subtle and may not be observable for years because trees are perennials and must therefore cope over time with the cumulative effects of multiple short- and long-term stresses. Reductions in the growth of annual rings observed in ponderosa, Jeffrey, and eastern white pine have been attributed to the exposure of the trees to O_3 over a period of 10 to 20 years (Miller and Elderman, 1977; Miller et al., 1982; McLaughlin et al., 1982; Benoit et al., 1982). Decline and dieback of red spruce in the northeastern United States and reduced growth rates of red spruce, balsam fir, and Fraser fir in central West Virginia and western Virginia also have been attributed to stresses, to which air pollution is a possible contributor, that began at least 20 years ago (Johnson and Siccama, 1983; Adams et al., 1985).

7.9.3 Effects of Ozone on Other Ecosystem Components and on Ecosystem Interactions

Evidence for the effects of ozone on other ecosystem components indicates that most are indirect, occurring chiefly as a result of the direct effects of ozone on trees and other producers. Significant alterations in producer species can change the ability of a species to compete and thus can influence the nature and direction of successional changes in the ecosystem. Likewise, significant alterations in producers can result in changes in the consumer and decomposer populations that depend on producers as their food source. Studies in the San Bernardino Mountain ecosystems in the 1970s have provided some evidence of successional shifts and of predisposition to infestation by pests and pathogens as the result of oxidant-induced changes in ponderosa and Jeffrey pines (see Section 7.9.4 below).

Marked morphological deterioration of the common lichen species, Hypogymnia enteromorpha, was documented in areas of the San Bernardino Mountains having high oxidant concentrations. A comparison of the species of lichens found growing on ponderosa and Jeffrey pine with collections from the early 1900's indicated the presence of 50 fewer species (Sigal and Nash, 1983).

McCool et al. (1979) and Parmeter et al. (1962) reported decreases in mycorrhizal infections and rootlets in ozone-stressed citrange (a citrus hybrid) and ponderosa pine, respectively. Mahoney (1982), on the other hand, found no evidence of impairment in the development of mycorrhizal associations in loblolly pine seedlings exposed to ozone plus sulfur dioxide; however, shoot dry weight was decreased by 12 percent.

The effects of ozone on mycorrhizae are of particular note here, since mycorrhizae are essential for the optimal development of most plants because of the functions they perform. Mycorrhizal fungi increase the solubility of minerals, improve the uptake of nutrients for host plants, protect roots against pathogens, produce plant growth hormones, and move carbohydrates from one plant to another (Hacskaylo, 1972). Ozone may disrupt the association between mycorrhizal fungi and plants, possibly by inhibiting photosynthesis and reducing the amounts of sugars and carbohydrates available for transfer from leaves of producers to the roots. Mycorrhizae are known to be sensitive to alterations in carbon allocation to the roots in host plants (Hacskaylo, 1973).

Because of the complex interactions among plants, pests, pathogens, and other biotic and abiotic factors, Laurence and Weinstein (1981) have emphasized the critical importance of examining pollutant-pathogen and pollant-insect interactions in determining the growth impact of a pollutant. Manion (1985) has emphasized the necessity of taking non-pollutant stresses, both biotic and abiotic, into account when attempting to attribute changes in forest ecosystems to air pollutants.

7.9.4 Effects of Ozone on Specific Ecosystems

One of the most thoroughly studied ecosystems in the United States is the mixed-conifer forest ecosystem in the San Bernardino Mountains of southern California. Sensitive plant species there began showing injury in the early 1950's (Miller and Elderman, 1977) and the source of the injury was identified as oxidants (ozone) in 1962 (Miller et al., 1963). In an inventory begun in 1968, Miller found that sensitive ponderosa and Jeffrey pines were being selectively removed by oxidant air pollution. Mortality of 8 and 10 percent was found in two respective populations of ponderosa pine studied between 1968 and 1972. Monitoring in that period showed ozone concentrations $\geq$0.08 ppm for $\geq$1300 hours, with concentrations rarely decreasing below 0.05 ppm at night near the crest of the mountain slope (Miller, 1973).

In a subsequent interdisciplinary study (1973 through 1978), biotic and abiotic components and ecosystem processes were examined. The ecosystem components most directly affected were various tree species, the fungal microflora of needles, and the foliose lichens on the bark of trees. In May through September, 1973 through 1978, 24-hr-average ozone concentrations ranged from about 0.03 to 0.04 ppm to about 0.10 to 0.12 ppm. (Monitoring was done by the Mast meter through 1974 and by the UV method from 1975 through 1978). Foliar injury on sensitive ponderosa and Jeffrey pine was observed when the 24-hr-average ozone concentrations were 0.05 to 0.06 ppm (Miller et al., 1982). Injury, decline, and death of these species were associated with the major ecosystem changes observed (Miller et al., 1982).

Growth reductions attributable to oxidant air pollution were calculated by McBride et al. (1975) for ponderosa pine saplings. Assuming 1910 to 1940 to be a period of low oxidant pollution and 1944 to 1974 a period of high oxidant pollution, they used radial growth increments (dbh) to calculate an oxidant-induced decrease in diameter of 40 percent. On the basis of the 3-year growth of saplings in filtered and nonfiltered air in portable greenhouses, they calculated oxidant-induced reductions of 26 percent in height growth (McBride et al., 1975). No standardized methods for determining tree ring widths were available at the time of this study.

Carbon flow and mineral nutrient cycling were influenced by the accumulation of litter under stands with the most severe needle injury and by defoliation, as well as by a reduction in the number of species and the population density of the fungi that normally colonize living needles and later participate in decomposition. The most likely result of heavy litter accumulation is a reduction in pine seedling establishment and greater establishment and growth of oxidant-tolerant understory species on some sites and oxidant-tolerant trees on other sites (Miller et al., 1982).

Changes in the energy available to trees influenced the biotic interactions, so that weakened ponderosa pines were more susceptible to attack by predators such as bark beetles and to pathogens such as root rot fungi (Stark and Cobb, 1969). Fewer western pine beetles were required to kill weakened trees (Dahlsten and Rowney, 1980); and stressed pines became more susceptible to root rot fungi (James et al., 1980b) and showed a decrease in mycorrhizal rootlets and their replacement by saprophytic fungi (Parmeter et al., 1962).

Accelerated rates of mortality of ponderosa and Jeffrey pine in the forest overstory, resulting from O_3 injury, root rot, and pine beetle attack, and in some cases, removal by fire, changed the basic structure of the forest ecosystem (Phase IV, Table 7-1; Bormann, 1985) by causing replacement of the dominant conifers with self-perpetuating, fire-adapted, O_3-tolerant shrub and oak species, which are considered less beneficial than the former pine forest and which inhibit reestablishment of conifers (Miller et al., 1982).

Injury to vegetation in other ecosystems has also been reported. Duchelle et al. (1983) found reductions in the growth and productivity of graminoid and forb vegetation in the Shenandoah National Park, where 1-hr ozone concentrations ranged from 0.08 to 0.10 ppm in the 3-year study period, with 1-hr concentrations >0.06 ppm occurring for 1218, 790, and 390 hours in 1979, 1980, and 1981, respectively. Treshow and Stewart (1973) fumigated species that grow in the Salt Lake Valley and the Wasatch Mountains in Utah and found key, dominant species to be ozone-sensitive. The National Park Service (1985) has recently reported ozone-induced injury to vegetation in the Santa Monica Mountains National Recreational Area, the Sequoia and Kings Canyon National Parks, Indiana Dunes National Lakeshore, Great Smoky Mountains National Park, and the Congaree Swamp National Monument. The impact of injury to vegetation in these ecosystems has not been appraised.

It should be emphasized that the relative importance of a given species in a given ecosystem must be considered in any assessment of the impact of ozone (or other stresses) on an ecosystem. Ozone has not had the impact on other ecosystems that it has had on the San Bernardino mixed-conifer forest because the plant species injured do not have a role equal in importance to the role of ponderosa and Jeffrey pines in the San Bernardino ecosystem.

7.9.5 Economic Valuation of Ecosystems

At the present time, economists and ecologists remain unable to devise a mutually acceptable framework for estimating the economic value of ecosystems. In addition, the credibility of any attempt to estimate at present the economic value of ecosystems would be diminished by a lack of scientific data (1) on the time-course of the manifestation of stress-induced effects on ecosystems, (2) on the point at which ecosystems lose the capacity for self-repair, and (3) on the points at which they begin to lose their ability to provide, respectively, priced and unpriced benefits to society. In addition, estimation of the economic losses that might be associated with the specific effects of ozone on ecosystems requires other data that are presently in short supply, i.e., better and more aerometric data and better and more data on additional variables, so that significant contributions from abiotic factors other than ozone, as well as from biotic factors, can be credibly estimated.

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8. EFFECTS OF OZONE AND OTHER PHOTOCHEMICAL OXIDANTS ON NONBIOLOGICAL MATERIALS

8.1 INTRODUCTION

Photochemical oxidants comprise various chemical species capable of reacting with a number of nonbiological materials. The nature and amount of damage to these materials can be approximated from oxidant concentrations (Chapter 5) and the rate constants of individual species. Unfortunately, there is virtually no information on the rates of reaction of photochemical oxidants other than ozone (O_3) on specific materials. Although ozone has been the primary photochemical oxidant studied, its prominence in the research literature does not necessarily indicate that it is the only important oxidant responsible for damaging materials. Under experimental conditions with certain chemical groups, OH radicals, which are far less abundant than ozone, have rates of reactivity much higher than those of ozone.

Nearly all research on photochemical oxidants has focused on economically important or abundant materials that are susceptible to oxidant damage. These include elastomers (natural rubber and certain synthetic polymers), textile fibers and dyes, and, to a lesser extent, paints. It has been shown that oxidants harden and embrittle elastomers, causing cracking and a loss in physical integrity. Damage, specifically by ozone, occurs mainly on the surface of these materials and is accelerated by mechanical stress. In the absence of ozone, oxidation by atmospheric oxygen still occurs, but at a slower rate and more in the bulk of the material. These effects have been known for years, and various antioxidants and other protective measures have been formulated to reduce the rates of attack. Oxidant exposure weakens certain textile fibers (i.e., reduces the breaking strength and increases the rate of wear) and changes the color of some dyes. Like elastomeric products, fibers and dyes particularly sensitive to ozone may be partly protected with resistant coatings or replaced with more durable formulations. Ultimately, these protective measures add to the cost of products. The effects of oxidants on paints are not defined well, but they may be similar to some of the effects on elastomers; damage from other gaseous pollutants, such as sulfur dioxide, tends to overshadow the role of ambient ozone in estimating paint damage.

To determine the actual damage to in-use materials, exposure must be estimated. As an example of the variables that must be taken into account, the ozone exposure of textile fibers and dyes used for clothing depends on the activity patterns of the wearer (i.e., time at home, at work, or outdoors), but the exposure of the same materials used for carpets and drapes involves only indoor air. Accordingly, a knowledge of product use and indoor/outdoor ozone gradients is essential when evaluating estimates of materials damage.

The literature selected for review in this section includes research previously reported in the 1978 criteria document (U.S. Environmental Protection Agency, 1978) and a limited number of references published before and after 1978. Of the twelve recent post-1978 references in this review, eight involve laboratory/field research, and four involve analyses that use previously published material. Because little recent work has been reported on the effects on nonbiological materials, reference to older studies is necessary for unity and coherence, for determining dose-response relationships, and for assessing economic impact. Technical areas considered in evaluating the cited studies include the type of study and exposure methods used (field versus laboratory; ambient conditions versus accelerated, artificial environments), the pollutant-monitoring and analytical methods used, the design and conditions of the experiment (e.g., inclusion of variables such as relative humidity and temperature), the statistical methods and level of significance, and the importance of the specific material studied. The absence of this type of information is noted in the text, when applicable. In addition, no attempt has been made to correlate aerometric data to materials in place, since the relationship between actual exposure and an unmatched set of air quality data is tenuous at best.

This assessment of the effects on nonbiological materials includes a review of the mechanisms of damage and protection; it also presents dose-response information from laboratory and field studies and evaluates previously reported economic assessments.

8.2 MECHANISMS OF OZONE ATTACK AND ANTIOZONANT PROTECTION

8.2.1 Elastomers

Most elastomeric materials found in the marketplace are composed of unsaturated, long-chain organic molecules. That is, the molecules contain carbon-carbon double bonds. Natural rubber and synthetic polymers/copolymers of butadiene, isoprene, and styrene account for the bulk of elastomer production for products such as automobile tires and protective electrical coverings used in outdoor environments (Mueller and Stickney, 1970). These types of compounds are susceptible to oxidation and are particularly susceptible to O_3 attack. In contrast, synthetic elastomers with saturated chemical structures, such as butyl rubber, polymers of silicones, ethylene, propylene, hypalon, and polyurethanes, have an inherent resistance to O_3 damage (Mueller and Stickney, 1970), but higher cost and limiting physical and chemical properties have constrained their use in outdoor environments.

The differences and similarities between simple oxidation (reaction with oxygen) and O_3 attack are described by Mueller and Stickney (1970). In the elastomer molecule, simple oxidation is postulated to proceed through the removal of a hydrogen atom from a carbon atom adjacent to a double bond; this is followed by the formation of a peroxy radical and subsequent radical reactions, which leads to chain scission and/or cross-linking (see Figure 8-1). Ozone is thought to attack by adding atoms directly across the double bond, forming a five-membered ring structure. This structure quickly rearranges (via Criegee ozonolysis) to form a zwitterion and an aldehyde (see Figure 8-2). Subsequent reactions of the zwitterion lead to a permanently oxidized elastomer.

Ozone damage, usually in the form of cracking, tends to be more a surface phenomenon than damage from simple oxidation. It is greatly accelerated by mechanical stress, which produces fresh surface area at crack boundaries. Simple oxidation, on the other hand, is slower; it occurs more in the bulk of a material, and it is less affected by the degree of stress.

At very high concentrations and high mechanical stress, O_3 damage can result in a large number of surface microcracks that produce a frosted appearance and mechanical weakening (Crabtree and Malm, 1956). Because, however, both simple oxidation and O_3 reactions lead to chain scission and chain cross-linking, the end result of both types of damage can be very similar in appearance. At pollutant concentrations and stress levels normally encountered outdoors (and in many indoor environments), the elastomer hardens or becomes brittle and cracked, which results in a loss of physical integrity. The influence of O_3 is evidenced primarily by the increased rate at which damage accumulates and by the degree of protection provided by various antioxidants and antiozonants.

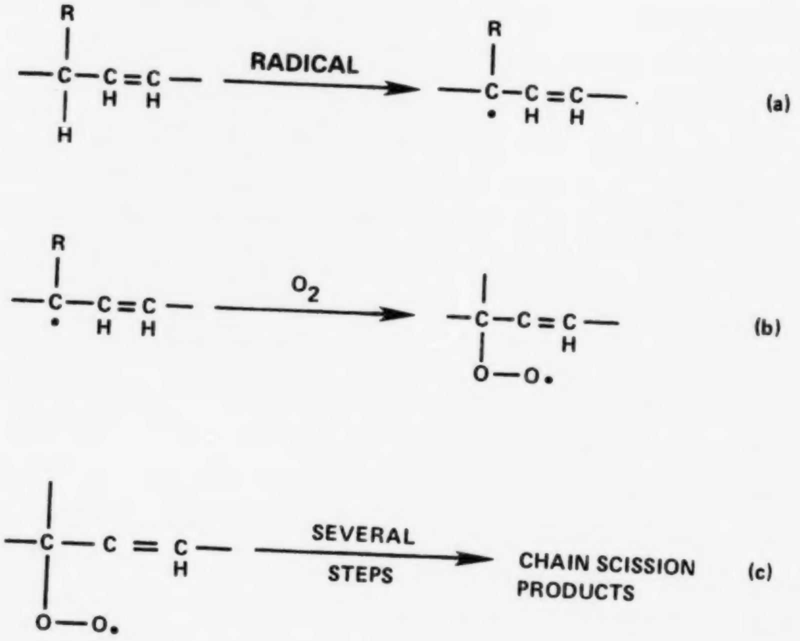
R
C
C = C
H H
RADICAL
(a)
O2
O—O•
(b)
SEVERAL
STEPS
CHAIN SCISSION PRODUCTS
(c)

Figure 8-1. Postulated mechanism for damage to elastomers by oxygen.

Source: Adapted from Mueller and Stickney (1970).

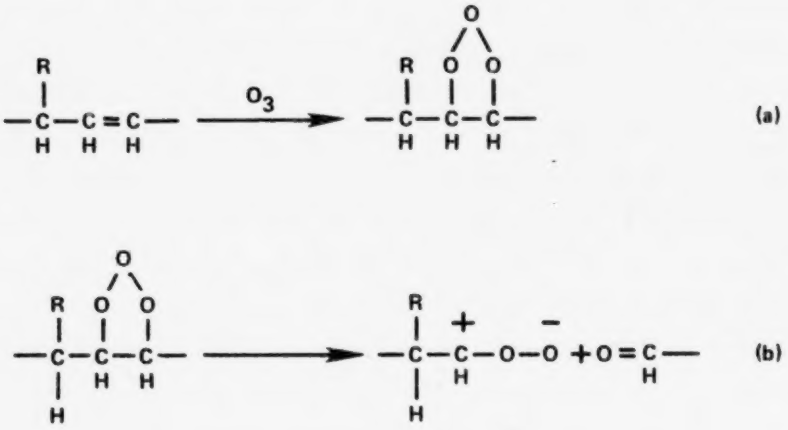

Figure 8-2. Postulated mechanism for damage to elastomers by ozone.

Source: Mueller and Stickney (1970).

According to Fisher (1957), work at the Rock Island Arsenal by R. F. Shaw, Z. T. Ossefa and W. J. Tonkey in 1954 led to the development of effective antioxidant additives to protect elastomers from O_3 degradation. Subsequently, antiozonants were generally incorporated into elastomeric formulations during mixing, and their protection was effective even when elastomers were stretched or flexed (Fisher, 1957; Mueller and Stickney, 1970).

Several theories have been advanced to explain the mechanism of antiozonant protection. As summarized by Andries and Diem (1974), these are the scavenger theory, the protective film theory, the recombination theory, and the self-healing film theory.

The scavenger theory suggests that the antiozonant diffuses to the surface, where it reacts with the O_3 at a faster rate than with the carbon-carbon double bonds of the rubber, thereby protecting the rubber sacrificially. The protective film theory also includes diffusion to the surface, but assumes that the resulting layer is less reactive with O_3 than is the rubber and thus constitutes a protective layer. The recombination theory proposes that the antiozonant prevents the propagation of the radical chain reactions initiated by O_3 attack. The self-healing film theory assumes that reaction products form on the surface and resist further degradation.

The work of Razumovskii and Batashova (1970) on the mechanism of protective action by the antiozonant N-phenyl-N'-isopropyl-p-phenylenediamine (PIPP) is most consistent with the scavenger mechanism. These investigators showed that O_3 reacts preferentially with PIPP at a ratio of three O_3 molecules per one PIPP molecule.

Andries et al. (1979), using carbon-black-loaded natural rubber (NR) compounds with and without antiozonants, attempted to distinguish among possible mechanisms with attenuated total reflectance spectroscopy and scanning electron microscopy. Their experiments indicated that a combination of the scavenger and protective film mechanisms best explains antiozonant protection. Examination of the surface of the rubber samples with antiozonant showed that only ozonized antioxidant and not ozonized rubber was present. This layer of ozonized antioxidant functioned as a relatively nonreactive film over the surface, preventing the O_3 from reaching and reacting with the rubber below.

In addition to reactive antiozonants, paraffinic and microcrystalline waxes are used to protect the elastomers in rubber products such as tires. Typically, the wax migrates to the surface of the rubber and forms a barrier against O_3 attack. The ability of the wax to protect the rubber depends on how well the wax migrates to the surface. This phenomenon, known as blooming, depends on a number of factors besides the characteristics of the wax. Dimauro et al. (1979) studied the ability of 18 waxes to protect rubber against degradation from O_3. Dimauro found that no wax by itself provided an optimal level of protection; blending with a reactive antiozonant was required. The paraffinic waxes protected best at lower exposure temperatures, and the microcrystalline waxes were more effective at higher temperatures. Wax blends, which combine the best effects of each type of wax, offered the best protection over a wide range of temperature. It was found, however, that wax alone can be detrimental to dynamic O_3 resistance. Wax can induce localized stresses in the rubber that can lead to premature rubber failure under dynamic testing conditions.

8.2.2 Textile Fibers and Dyes

Damage to textile fibers from O_3 is difficult to distinguish from that caused by oxidation by oxygen. Reduction in breaking strength and an increased rate of wear are the types of damage most commonly observed. Cellulose-based fibers, acrylic fibers, and nylon fibers are affected by O_3, and modacrylic and polyester fibers have been shown to be relatively unaffected by the levels of O_3 normally experienced in the ambient atmosphere (Zeronian et al., 1971). As stated by Bogaty et al. (1952), however, for most uses of textile fibers the action of O_3 or oxygen is less important in product lifetime than physical abrasion, biological degradation, soiling, fashion, and other factors. Accordingly, the economic significance of O_3 damage to textile fibers is relatively low, and the differences in the mechanisms of attack are not important. Nevertheless, an important property of textile products is appearance or color; O_3 reacts with a number of dyes to cause fading or changes in color.

Oxidation is the fundamental chemical reaction leading to color change in dyed fibers exposed to O_3. Compared with other oxidizing pollutants such as nitrogen oxides, O_3 often leads to a higher degree of oxidation and thus to different types of color changes. Terms such as O-fading and Gulf Coast fading have been given to some of the unique color changes attributed to reactions with O_3.

Figure 8-3 illustrates the reaction of Disperse Blue #3 with O_3 and with nitrogen oxides (Haylock and Rush, 1976). Although the nitrogen oxides removed an alkylamine side chain, O_3 attacked the quinoid portion of the molecule,

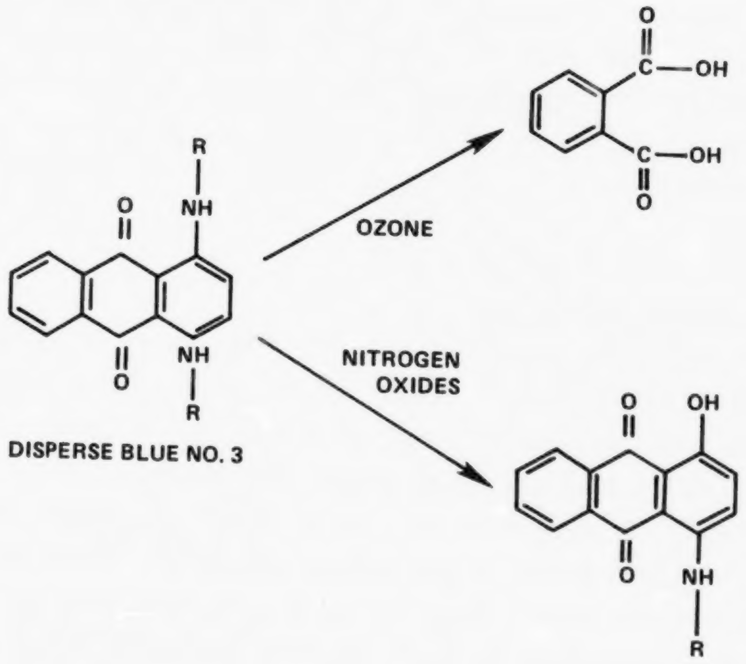
R
NH
O
O
NH
R
DISPERSE BLUE NO. 3
OZONE
NITROGEN OXIDES
C—OH
C—OH
OH
NH
R

Figure 8-3. Reaction of anthraquinone dyes with ozone and with nitrogen oxides.

Source: Haylock and Rush (1976).

completely rupturing the ring system chromophore and oxidizing the dye to phthalic acid, which is colorless.

The reactions between various chemical categories of dyestuffs and O_3 is influenced not only by the properties of the dye but also by the chemical nature of the fiber to which the dye is applied and the manner in which the dye is applied. Additional factors include the presence of protective agents; synergistic or additive effects of temperature, air moisture, and other pollutants; and even the degree of strain of the base fiber caused by folding or creasing. For example, in a study of O_3 fading of anthraquinone dyes on nylon, Haylock and Rush (1976, 1978) found that fiber properties such as cross-section shape, draw ratio, and the degree of steam heat setting had significant effects on the rate and severity of O_3 damage, even for chemically identical systems. Given this complexity and sensitivity, it is not practical to relate a specific mechanism of damage to a broad class of damage situations. Furthermore, it may not be necessary to do so. In most cases, some combination of dye, fibers, and protective treatments can eliminate the major problems caused by O_3 exposure and still provide the range of colors desired in the final products.

8.2.3 Paint

The mechanisms of paint damage caused by O_3 have not been defined well. Damage is probably related to oxidation of the organic binders that hold the pigment and form the protective seal over the surface. Damage is likely to be similar to that of elastomers; that is, embrittlement and cracking as the result of chain scission and cross-linking. The data available on O_3 damage to paints, however, come primarily from studies of surface erosion caused by gaseous pollutants. Because the polymeric structure of dried paint film is significantly different from that of an elastomer under elongation stress, direct comparisons should be made with great caution.

8.2.4 Other Materials

Although the effects of oxidants on other materials have been examined by several investigators, most of the limited information is qualitative and centers on mechanisms of effects. Sanderson (1975), in a review of the effects of photochemical smog on materials, included possible effects on plastic and asphalt. The indicated impacts have little direct applicability, however, because these effects were recorded in a laboratory environment at extremely high O_3 levels.

Haynie and Upham (1971) reported a possible beneficial effect of photochemical oxidants on the corrosion behavior of steel on the basis of field study data. Laboratory studies, however, did not show any statistically significant effect of O_3 on steel corrosion.

Polyethylene, commonly used as electrical insulating material, may be adversely affected by ambient O_3 concentrations. Laboratory studies (National Research Council, 1977) have demonstrated by means of infrared and other techniques that terminal double bonds in polyethylene end groups are attacked by "ozonized" oxygen to form carboxylic acid groups and, through ruptures in the polymer chain, to produce short-chain dicarboxylic acids.

It is also known that atomic oxygen reacts with polyethylene at room temperature to produce a loss in weight and some morphologic changes. The work of Trozzolo and Winslow (1968) and Kaplan and Kelleher (1970) suggests that singlet oxygen also interacts with polyethylene to form hydroperoxides. Laboratory studies suggest that hydroperoxides may be the dominant oxidants that attack polyethylene or other materials in ambient air.

Despite the known interactions of oxidants with polyethylene and other polyolefins to form intermediate peroxy radicals, there is no evidence that the chemical reactions go far beyond the surface. It is believed that the effects of atmospheric O_3 on polyethylene insulation and other polyethylene products are negligible in comparison with the embrittlement caused by a combination of oxygen and sunlight. The mechanisms by which this embrittlement occurs probably involve sensitization to oxidation by absorption of ultraviolet (UV) radiation, by residual hydroperoxy and carbonyl groups in the polymer, and by surface deposits of aromatic sensitizers from polluted air. Deterioration of the electrical insulating properties of polyethylene by oxidation in some environments cannot be attributed to ambient O_3.

8.3 DOSE-RESPONSE DATA

Most dose-response studies are criticized for their reliance on artificial environments (laboratory settings) that do not contain all the critical variables encountered under ambient conditions. Scientists realize the limitations of laboratory tests; no model could simulate conditions identical to an ambient environment. Nevertheless, many laboratory tests have represented the outdoor environment to some extent, and the findings from these tests have been used in conjunction with field tests to estimate the nature and amount of damage to materials.

8.3.1 Elastomer Cracking

Hofmann and Miller (1969) demonstrated correlations between laboratory tests and the actual service use of passenger vehicle tires in the Los Angeles area. Basically, three laboratory test methods were used (Table 8-1): indoor and outdoor belt flex, indoor and outdoor wheel, and stress relaxation. They found that the behavior of rubber exposed to O_3 under laboratory conditions correlated well with the service behavior of tires in localities where atmospheric O_3 concentrations were high. The relative susceptibilities of different formulations of white sidewall rubber were generally similar, whether exposed under laboratory conditions to as much as 0.5 ppm (980 $\mu g/m^3$) of O_3 or exposed in the ambient air of the Los Angeles area, which had annual average O_3 concentrations near 0.04 ppm (80 $\mu g/m^3$) (U.S. Department of Health, Education, and Welfare, 1970). The exact exposure times, pollutant measurement methods, and statistical analyses were not reported.

Bradley and Haagen-Smit (1951) evaluated a natural rubber (NR) formulation for susceptibility to O_3 cracking. Strips were strained approximately 100 percent by bending and then exposed in a small chamber to 40,000 mg/m^3 (20,000 ppm) of O_3; these specimens cracked almost instantaneously and broke completely within 1 sec. When these NR formulations were exposed to lower concentrations of O_3, different time periods were required for cracks to develop, as shown in Figure 8-4, and this action increased with increasing temperature. Humidity and sunlight had little influence on cracking rate. According to the data in this figure, the initiation of cracks and subsequent deepening are controlled by the dose of O_3 (concentration x time).

Meyer and Sommer (1957) exposed thin polybutadiene specimens to constant load, ambient room air, and O_3. Specimens exposed in the summer to average O_3 concentrations of about 0.048 ppm (94 $\mu g/m^3$) broke after 150 to 250 hr. In the fall, at average O_3 concentrations of 0.042 ppm (82 $\mu g/m^3$), specimens failed after exposures of 400 to 500 hr. In the winter, at average O_3 concentrations of 0.024 ppm ($\sim$47 $\mu g/m^3$), failures occurred between 500 and 700 hr. Like the Bradley and Haagen-Smit study, these data also show the strong dependence of breakage on O_3 dose over the average time of exposure at which failure occurred (average concentrations x time), but not in the same linear fashion.

TABLE 8-1. TIRE INDUSTRY EXPOSURE TESTS[a]

Test	Strain	Conditions	Reasons for Use
Belt flexing	Dynamic at 4500 to 7500 flexures per hour	Ozone chamber at 0.35 to 0.50 ppm, or outdoors for several days	Rapid evaluation, variable conditions for screening sidewall compounds
Stress relaxation	Dynamic or static; 25 percent extension at 90 cpm	Ozone cabinet at 0.25 to 0.50 ppm for 16-hr increments	Rapid evaluation, variable conditions for screening sidewall compounds
Outdoor wheel	Dynamic and static; variable loads, inflation, and speed	Los Angeles area, high ozone for several weeks	Quicker and cheaper than tire testing on autos in actual service
Indoor wheel	Dynamic and static; variable loads, inflation, and speed	Large ozone chamber at 0.01 to 0.35 ppm and -20 to 100° F, for days TO weeks	Strain most similar to actual service, quicker and cheaper than outdoor wheel
Tire tests on vehicles	Dynamic and static; variable loads, inflation, and speed	Extreme and typical service areas for 1/2 to 2 yr	Ultimate test of product life

[a] Adapted from Hofmann and Miller (1964).

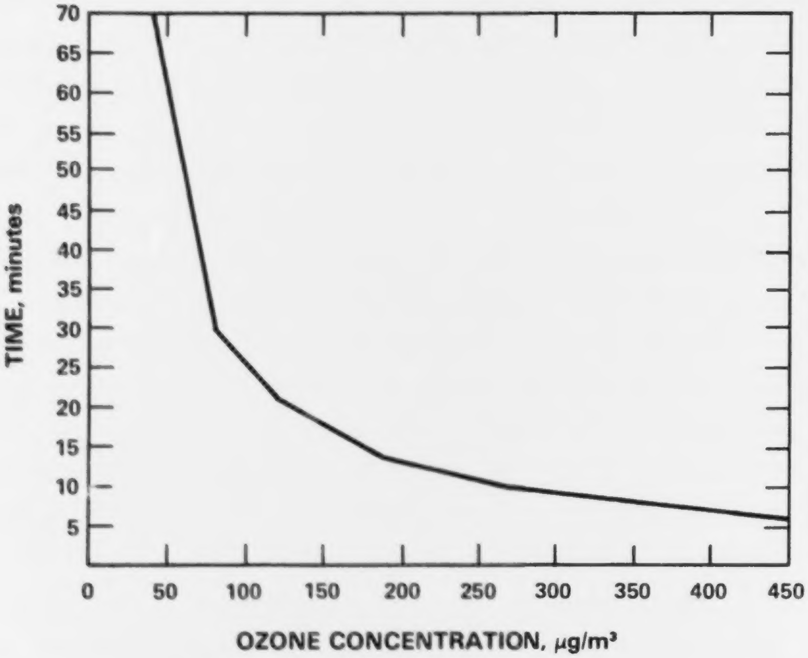

Figure 8-4. Relationship of cracking in rubber and ozone concentration: time to first sign of cracking at 4x magnification in natural rubber samples stressed at 100%.

Source: Bradley and Haagen-Smit (1951).

Dose-response levels in this study are noted parenthetically for the following concentrations: 0.048 ppm (7.2-12 ppm x hr); 0.042 ppm (16.8-21 ppm x hr); 0.024 ppm (12-16.8 ppm x hr).

In describing a new test method for evaluating the O_3 sensitivity of elastomers, Edwards and Storey (1959) presented data demonstrating the O_3 resistance of two styrene-butadiene rubber (SBR) compounds (Polysar S and Polysar Krylene). Both compounds were exposed without and with different levels of antiozonant protection to 0.25 ± 0.05 ppm of O_3 (490 ± 98 $\mu g/m^3$) at 120°F (49°C) under 100 percent strain twice the original sample length. The results are presented in Table 8-2. Without antiozonants, a linear relationship is indicated between O_3 dose (ppm/hr) and cracking depth. The coefficient of determination for the linear regression for both materials was 0.98 compared with 0.92 for the exponential fit. Note that the Polysar S compound displays much greater resistance to the effects of O_3 than does the Polysar Krylene compound. Nevertheless, increasing the amount of antiozonants significantly reduced the rate of cracking for both in a dose-related manner.

Haynie et al. (1976) conducted a chamber study to evaluate the effects of various pollutants, including O_3, on several materials. In one part of the study, white sidewall specimens from a top-quality, steel-belted radial tire were exposed (strained at 10 and 20 percent) for 250, 500, and 1000 hr to O_3 concentrations of 160 $\mu g/m^3$ and 1000 $\mu g/m^3$. The O_3 level was found to be statistically significant in the rate of cracking of this rubber. However, cracking rates are not directly proportional to O_3 concentrations for these two levels. The average results with respect to strain and O_3 level are given in Table 8-3.

Using the mean cracking rate calculated after long-term (1000 hr) exposure to conditions representative of the primary air quality standard for O_3 and the annual average standard for nitrogen dioxide (NO_2), Haynie et al. (1976) concluded that it would take a minimum of 2.5 years for a crack to penetrate to the cord depth. Additional time would be necessary to attack the cords. For this particular premium tire, therefore, sidewall failure from O_3 damage does not appear to be the cause of reduced tire life. However, the casing might have questionable value for retreading. Tread wear, rather than sidewall failure, probably determines the life of a typical rubber tire, and the rubber used in tire treads is generally more resistant to O_3 than that in the sidewalls.

TABLE 8-2. EFFECTS OF OZONE ON DIFFERENT SBR POLYMERS CONTAINING VARIOUS ANTIOZONANT CONCENTRATIONS

Polymer	Antiozonant, pph	Crack depth, 10^{-3} in., at hr of exposure				Cracking depth rate	
		19	27	43	51	10^{-4} in./hr	μm/hr
Polysar S ("Hot" SBR)	0.0	1.37	2.42	4.20	4.65	0.92	2.34
	0.5	0.95	1.90	3.10	3.52	0.69	1.75
	1.0	0.50	0.75	1.47	1.95	0.35	0.89
	2.0	0.25	0.25	0.45	0.78	0.13	0.33
Polysar Krylene ("Cold" SBR)	0.0	2.17	4.52	7.25	7.90	1.58	4.01
	0.5	1.25	2.02	3.75	4.50	0.85	2.16
	1.0	1.05	1.50	2.24	2.90	0.57	1.45
	2.0	0.50	0.75	1.00	1.18	0.24	0.61

Source: Edwards and Storey (1959).

TABLE 8-3. CRACKING RATES OF WHITE SIDEWALL TIRE SPECIMENS

Ozone concentration $\mu g/m^3$ (ppm)	Strain percent	Mean cracking rate ± standard deviation, mm/yr	μm/hr
160 (0.08)	10	11.66 ± 7.32	1.33
	20	17.00 ± 10.45	1.94
1000 (0.5)	10	15.38 ± 5.38	1.76
	20	25.74 ± 8.23	2.94

Source: Haynie et al. (1976).

Veith and Evans (1980) investigated the effect of atmospheric pressure on the cracking rate of rubber as tested in O_3 chambers. It was found that a change in barometric pressure alters the rate of cracking. Interlaboratory comparisons were made among facilities at different geographic elevations and thus significantly different atmospheric pressures. It was found that a 16-percent difference in cracking rate or in the extent of cracking at a fixed O_3 concentration could occur. In an effort to correct the problem and standardize the testing techniques, Veith and Evans (1980) recommended that O_3 content in accelerated chamber testing be expressed in terms of O_3 partial pressure (in Pa units) rather than simply in terms of concentrations.

Gandslandt and Svensson (1980) evaluated the stress test methodology used to estimate the O_3 resistance of rubber compounds. This test measures the decrease in the isoelastic force of stressed rubber exposed to O_3. The authors suggested that materials should be prestressed in an O_3-free atmosphere for at least 72 hr before testing, because the complicating effects of the natural relaxation of the isoelastic force constant of the material decreases exponentially with time. The effects of this natural relaxation mechanism become insignificant after 2 to 3 days of prestressing compared to the effects caused by O_3 cracking.

Ten different mixtures of three rubber compounds, NR, SBR, and CR (a compound not defined by the authors), were tested with the isoelastic force method (Gandslandt and Svensson, 1980). The O_3 protection afforded each rubber formulation is summarized in Table 8-4. After a relaxation time of 70 hr in an O_3-free atmosphere (2 hr less than their prescribed criteria for sample exposure), the samples at 50-percent elongation were exposed to O_3 concentrations of 0.5 ppm (980 $\mu g/m^3$) at 30°C. The time to 10-percent and 20-percent relaxation of the isoelastic force in the rubber test samples was used to gauge the O_3 resistance of the formulation. Compounds GL 2073 B, SS 203, and SS 200 C showed greatest resistance to the effects of O_3, and those formulations that were unprotected (GL 2073 D, SS 200 B, SS 202 A, SS 203) and the formulations protected only by paraffin wax (GL 2073 G) demonstrated the least resistance to O_3 attack. The testing showed great variety in the kinds of visible cracking effects as a result of the exposure. The compounds with no protection often showed a large number of small cracks over the entire surface of the material, but those compounds protected by a combination of wax and antiozonant or by wax alone sometimes showed only a single

TABLE 8-4. PROTECTION OF TESTED RUBBER MATERIALS

Rubber formulation		Unprotected	Protected	
			Wax	Antiozonant
GL 2073	B, C		X	X
	G		X	
	D	X		
SS 200	A, C		X	X
	B	X		
SS 202	A	X		
	B		X	X
SS 203		X		

Source: Gandslandt and Svensson (1980).

crack, which grew rapidly. These effects are demonstrated in Figure 8-5. Compounds SS 202 B (Figure 8-5a) and SS 200 C (Figure 8-5b), both protected with wax and antiozonant, showed fairly good resistance when gauged by the 10-percent and 20-percent stress relaxation tests but failed after approximately 50 hr and 58 hr of exposure, respectively. On the other hand, compounds SS 203 and SS 200 A, both unprotected, exhibited small surface cracking and outlasted some of the protected compounds. Moreover, protection with wax and antiozonant may afford long-term protection, but when one crack appears, it can grow rapidly and cut off the test piece, as shown in Figure 8-5b.

Davies (1979) reported on the effects of ozone and other environmental factors on interply adhesion of natural and synthetic rubber compounds. Excellent adhesion of plies is essential to the proper manufacturing of tires. The rubber strips must make interlocking contact at the joint boundary or the strength of the product will be inadequate. Ozone attack on synthetic polyisoprene and polybutadiene produces a surface layer of ozonides. With NR, the film consists of ozonides and carbonyl groups (Andries and Diem, 1974; Andries et al., 1979). The results of the Davies (1979) tests indicated that before curing, the adhesion of SBR compounds is unaffected by exposure to O_3 concentrations of 0.15 ppm (294 $\mu g/m^3$), but the adhesion of the NR/SBR blend decreases by approximately 30 percent. Large reductions (on the order of 70 percent) in adhesion between plies were noted with the NR compounds; even exposure for a

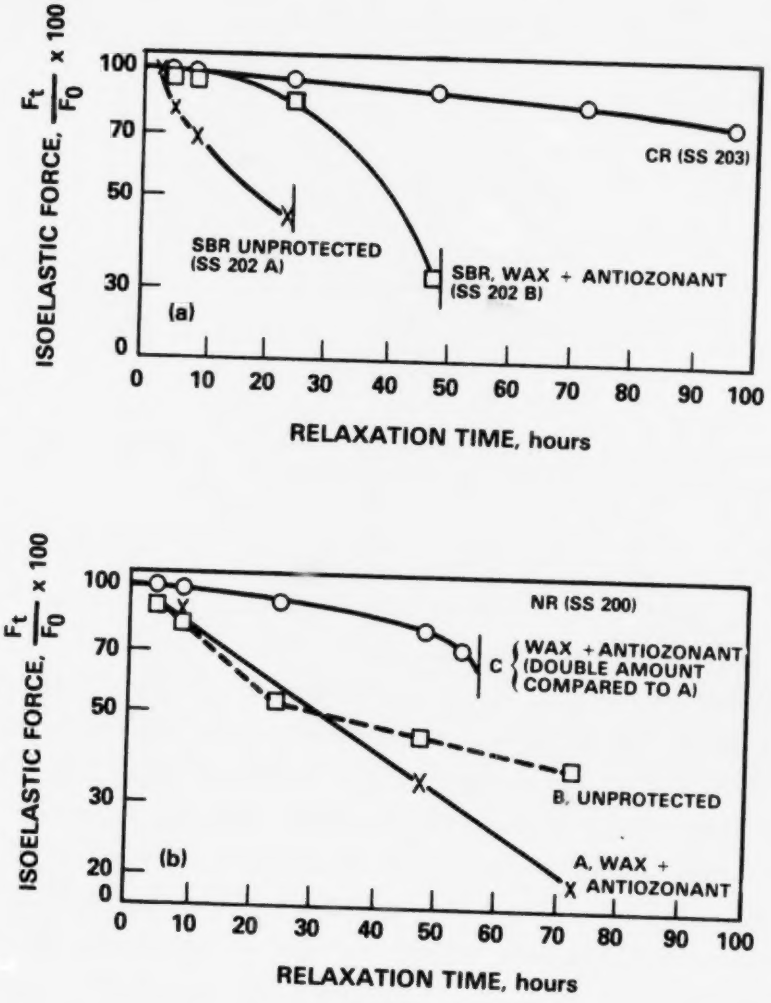

Figure 8-5. Relaxation of rubber compounds in O_3 is affected by the combination of rubber formulation and type of O_3 protection. Compounds were tested at O_3 concentration, 0.5 ppm (980 $\mu g/m^3$); temperature, 30°C; elongation, 50%. Vertical line at the end of a curve means total failure, and vertical axis represents relaxation where F_0 is the initial force; F_t is the force after time, t.

Source: Gandslandt and Svenson (1980).

few hours at 0.05 ppm reduced adhesion considerably. The adhesion tests on cured NR, SBR, and isoprene rubber (IR) compounds after exposure to various levels of O_3 and humidity are summarized in Table 8-5. The adhesion of the SBR compound is superior to that of the other two compounds, which were greatly affected by increased RH.

TABLE 8-5. EFFECT OF OZONE AND HUMIDITY ON INTERPLY ADHESION[a]

		Final adhesion[b]		
Compound	Initial adhesion	0.15 ppm O_3 (294 μg/m^3), 30% RH	0.25 ppm O_3 (490 μg/m^3), 30% RH	0.15 ppm O_3 (294 μg/m^3), 60% RH
NR	5	2-3	1	1
IR	5	4-5	2-1	1
SBR	5	4-5	3-4	3-4

[a] Adhesion is rated from 1 (bad) to 5 (excellent), based on a visual scale standardized by the authors.

[b] All exposures were 16 hr in duration.

Source: Adapted from Davies (1979).

Davies examined antiozonants, antioxidants, and fast-blooming waxes as means of protecting NR compounds from sunlight and O_3 attack and the subsequent development of the films that lead to poor adhesion between plies. The results of these evaluations are presented in Table 8-6. Of the samples exposed after 16 hr at O_3 concentrations of 0.15 ppm (294 μg/m^3), only those protected by the fast-blooming waxes were found to resist O_3 and have excellent adhesion between plies (Table 8-6). Antiozonants and antioxidants in the NR did not aid interply adhesion (Table 8-6). Davies (1979) theorized that antiozonants and antioxidants react with ozonized rubber and form a protective film against further attack by O_3. However, this film also apparently acts as a barrier to proper adhesion between plies. Davies noted that after exposure to sunlight alone, the antioxidants generally maintained good adhesions, but the waxes gave only fair protection. He concluded that the combination of a fast-blooming wax and an effective antioxidant or antiozonant is necessary to protect NR from O_3 attack and sunlight.

TABLE 8-6. EFFECT OF ANTIOZONANTS, ANTIOXIDANTS, AND FAST-BLOOMING WAXES ON INTERPLY ADHESION IN NATURAL RUBBER[a]

Antiozonant[b,d]	Rating[c]
Untreated	1
ETMQ	1
6 PPD	1
1 PPD	1
77 PPD	1
TBMP	2
TMQ	2
Wax 1	5
Wax 2	5

[a] Ozone resistance rated from 1 (bad) to 5 (excellent), based on a visual scale standardized by the author.

[b] All substances were given an initial rating of 5.

[c] Rating assigned after 16-hr exposure to 0.15 ppm (294 μg/m³) of O_3.

[d] See appendix for explanation of abbreviations.

Source: Davies (1979).

Wenghoefer (1974) studied the effects of O_3 on adhesion and the climatic sensitivity of tire cords dipped in resorcinal-formaldehyde latex (RFL). Climatic sensitivity was described as summer sickness, a problem affecting cords primarily during hot, humid weather. Many fibers and dip formulations were studied to determine their sensitivity to O_3, humidity, nitrogen dioxide (NO_2), UV light, and heat. Wenghoefer exposed these materials at a constant temperature of 100°F (37.8°C) to O_3 levels that varied between 0 and 1.5 ppm (0 and 2940 $\mu g/m^3$) and to relative humidity (RH) levels ranging from 20 to 90 percent. Adhesion deteriorated from changes in surface properties of the RFL-dipped cords as a result of exposure to O_3, humidity, UV light, and heat. The adhesion losses from O_3 and the combined effects of O_3 and humidity were most notable in the first 6 hr of exposure. The detrimental effects of heat, NO_2, and the synergistic interaction of NO_2 and humidity were much less pronounced. Table 8-7 summarizes the elastomer dose-response studies.

8.3.2 Dye Fading

Color fading of certain textile dyes has been attributed to the effects of ambient O_3. Although NO_2 was originally identified as the pollutant most

TABLE 8-7. DOSE-RESPONSE STUDIES ON EFFECTS OF OZONE ON ELASTOMERS

Conditions	Material/Product	Pollutant	Concentration, ppm	Measurement method	Exposure	Environmental variables	Dose, ppm-hr	Effects	Comment	Reference
Laboratory/ field	Automotive tires	Ozone	0.25 to 0.5	NA	NA	Tires under stress	-	Cracking of white side wall	Purpose was to correlate lab- and field tests.	Hoffman and Miller (1969)
		Ambient air	0.04 O_3 (annual average)	NA	>1 yr	Los Angeles environment; actual service use	>350	Positive correlation between laboratory and ambient air tests	Exposure time, detailed pollutant measurements, and statistical analyses were not reported.	
Laboratory	Vulcanized rubber strips	Ozone	0.02 to 0.46	NA	3 to 65 min	Physical stress	~0.02 to 0.03	Surface cracking	Test was designed to establish dose/response curves on O_3-sensitive rubber for use as an analytical method.	Bradley and Haagen-Smit (1951)
Controlled field	Rubber tires and various polymers	Ambient air	0.023 to 0.048 O_3.	NA	150 to 700 hr	Physical stress and ambient environment	9 to 20	Time of cracking	Cracking occurred over a broad range of values and was related to stress.	Meyer and Sommer (1957)
Laboratory	SBR: Plysar S Plysar Krylene with and without antiozonants	Ozone	0.25	NA	19 to 51 hr	120°F, 100% strain	4.75 to 12.75	Percent antiozonant was related to cracking depth rate	Demonstrated dose/response linear relationship for ozone on unprotected rubber.	Edwards and Storey (1959)

TABLE 8-7. DOSE-RESPONSE STUDIES ON EFFECTS OF OZONE ON ELASTOMERS (continued)

Conditions	Material/Product	Pollutant	Concentration, ppm	Measurement method	Exposure	Environmental variables	Dose, ppm-hr	Effects	Comment	Reference
Laboratory	White sidewall tire specimens	Ozone	0.08 to 0.5	NA	250 to 1000 hrs	10 and 20% strain.	20 to 500	Mean cracking rates were determined for different stress and ozone levels.	Detailed data not available to verify author's statement that 2-1/2 years of ambient conditions were required for ozone cracks to penetrate cord depth.	Haynie et al. (1976)
Laboratory	Ten different NR, SBR, CR formulations with and without protection	Ozone	0.5	NA	Up to 300 hr	30°C	Up to 50	Time to 10 to 20% relaxation	Both formulation and protection affected relaxation.	Gandslandt and Svensson (1980)
Laboratory	Several NR/SBR blends with and without protection	Ozone	0.05 to 0.15	NA	~3 to 16 hr	Sunlight, humidity	~0.15-2.4	Interply adhesion affected at 0.05 ppm and above	Both waxes and antiozonants needed for protection against sunlight plus ozone.	Davies (1979)
Laboratory	Tire cords (66 nylon; Dacron polyester; Kevlar aramid)	Ozone	0 to 1.5	NA	0 to 48 hr	UV light; heat (100°C); RH (20-90%); NO_2	up to 72	RFL adhesion loss occurred primarily during 6-hr exposure to high RH and 0.2 ppm O_3.	Synergism between O_3 and RH; RFL deterioration occurred at surface.	Wenghoefer (1974)
		Nitrogen dioxide	0 to 20	NA						

important to color fading, the effects of O_3 were noted by Salvin and Walker (1955) nearly three decades ago. The phenomenon was termed O-fading. The primary products affected were permanent press garments (polyester and cotton) and nylon carpeting. In permanent press garments, dye fading occurs primarily at the creases and folds. The fading of nylon carpeting occurs in the presence of high RH and depends on the dyes used. Ozone fading most affected the blue and red disperse dyes of the anthraquinone series but not the azo series of dyes.

Salvin and Walker (1955) tested disperse dyes that were resistant to the effects of nitrogen oxides. They exposed a series of drapery products to confirm their resistance to the dye fading that was thought to be attributable to NO_2. Different types of dyes ranging in vulnerability to nitrogen oxides were exposed in Pittsburgh, Pennsylvania (an urban region of high NO_2 concentrations), and Ames, Iowa (a suburban area with low NO_2 concentrations). After 6 months of exposure, the investigators found that NO_2-resistant dyes had performed well in Pittsburgh but poorly in Ames, indicating the influence of another fading agent. By using a combination of laboratory chamber studies and outdoor exposure, Salvin and Walker (1955) demonstrated that O_3 was the pollutant responsible for the change. Blue anthraquinone dyes and certain red anthraquinone dyes were markedly bleached after exposure to just 0.1 ppm (196 $\mu g/m^3$) of O_3. Azo red and yellow dyestuffs and diphenylamine yellow dyes were shown to be resistant to fading at these concentrations, also confirming the results of the field study. The use of known antiozonants, such as diphenylethylenediamine and diallyl phthalate, in combination with disperse blue dyes was effective against O_3 fading, thus providing additional evidence of the effects of O_3 on dyed fabrics.

To explain much of the fading of certain dyed fabrics during lightfastness testing and service exposure trials, Schmitt (1960, 1962) also invoked the concept of O_3 fading. In studies to demonstrate colorfastness of certain dyes when exposed to sunlight, Schmitt exposed 38 color specimens for 12 months at Phoenix, Arizona, and Sarasota, Florida, and for 7 months in Chicago, Illinois. Specimens exposed included direct dyes on cotton, acid dyes on nylon, acid dyes on wool, disperse dyes on acetate, disperse dyes on acrilan, disperse dyes on dynel, acid dyes on dynel, cationic dyes on orlon, and disperse dyes on dacron.

Each specimen was exposed to a predetermined amount of direct sunlight, measured by a pyroheliometer, and then examined in the laboratory to measure the amount of fading. Schmitt found that samples given equal amounts of sun exposure tended to fade more in Florida than in Arizona. He concluded that the higher RH was a contributory factor and that atmospheric contaminants were the principal factor in accelerated fading. Schmitt also exposed certain dyed fabrics in covered test frames where the effect of sunlight would be eliminated. After 24 days of exposure in Florida, Schmitt found that even in covered frames fading was of the same magnitude as noted with samples exposed to sunlight. His work also demonstrated the importance of RH in the dye-fading mechanism by suggesting that the increased moisture content of the fibers promoted and accelerated the absorption and reaction of pollutants with vulnerable dyes.

Ajax et al. (1967) summarized the results of a study of 69 dye-fabric combinations that were exposed outdoors in light-free cabinets at 11 sites. These sites were Sarasota, Florida; Phoenix, Arizona; Cincinnati, Ohio; and four urban-rural combinations: Chicago and Argonne, Illinois; Washington, D.C., and Poolesville, Maryland; Los Angeles and Santa Paula, California; and Tacoma and Purdy, Washington. Among those fabrics exhibiting a high degree of fading at both urban and rural sites in the first 6 months, fading was much greater at the urban sites than at the rural sites. The samples exposed in Phoenix, Sarasota, and Purdy showed the lowest amount of fading, which indicated that humidity and temperature are not, by themselves, the primary factors in fading. The highest fading rate occurred in samples exposed in Los Angeles, Chicago, and Washington, D.C. In addition, there was a marked seasonal variation in the test results, with greater fading during the spring and summer seasons. Generally, the results correspond with seasonal peaks in O_3 concentrations. Editorial problems, however, between the text and tabular material tend to confuse the authors' discussion.

Ajax and coworkers also exposed the fabrics to irradiated and nonirradiated auto exhaust with and without sulfur dioxide (SO_2) for 9 hr/day for six consecutive days. From the results of this chamber study, they noted that "photochemically produced byproducts of automobile exhaust are a prime cause of fading compared to fading caused by nonirradiated auto exhaust or by clean air with sulfur dioxide added." In the presence of SO_2, however, a more than additive effect was seen in the dye fading tests for both chamber and field studies. Although their conclusions concerning ozone itself are easily substantiated in the research literature, the O_3 levels measured in their chamber are questionable. The daily 9-hr average O_3 concentrations (measured by neutral KI, Mast instrument) were identical for irradiated (UV) and nonirradiated exhaust (0.02 ppm); irradiated exhaust plus SO_2 produced 0.55 ppm of O_3.

Beloin (1972, 1973) investigated the effects of air pollution on various dyed textiles by conducting field and controlled-environment laboratory studies. For the field study, a wide range of dyed fabric was exposed in light-tight cabinets at the same four urban and four rural sites used in the Ajax studies. The study was carried out over a 2-year period, in eight consecutive 3-month seasonal exposure periods. Color change data and air pollution and weather measurements were analyzed to identify the factors that caused fading. About two-thirds of the fabrics studied showed appreciable fading. Most of these fabrics faded significantly more at urban sites than at rural sites, and the amount of fading varied among metropolitan areas and seasons. Samples exposed in Chicago and Los Angeles demonstrated the greatest degree of fading, and those exposed in Purdy, Washington, and Phoenix showed the least amount. The small amount of fading evidenced by the samples exposed at extreme temperatures and/or humidity indicated that these factors by themselves have no effect on fading. The sample also showed some seasonal variations in fading. In areas of high oxidant concentration, maximum fading occurred primarily in summer and fall. Fabrics exposed in Chicago, where SO_2 concentrations are higher in the winter, showed greater fading during this season.

The results of the outdoor fading study were used in a multiple regression analysis, which examined fading as a function of six independent variables (NO_2, SO_2, O_3, nitrogen oxide, temperature, and humidity). After eliminating those fabrics that developed only trace fading and those for which the regression was not significant, the analysis focused on 25 fabric dye samples, 23 of which showed SO_2 to be a significant variable. Ozone was also a significant contributor to fading of eight dyed fabrics and NO_2 to fading of seven dyed fabrics. The dominance of SO_2 as a factor in fading may have been complicated by soiling.

The laboratory study was designed to assess the effects of air pollutants, temperature, and RH on the colorfastness of 30 samples selected from those exposed during the field study. Fabric samples were exposed to two concentrations of O_3: 0.05 ppm (98 $\mu g/m^3$) and 0.50 ppm (980 $\mu g/m^3$). The laboratory studies demonstrated that high O_3 levels produced more significant fading in more fabric samples than did low levels. Visible fading did occur in about one-third of the sensitive fabrics exposed to O_3 concentrations of 0.05 ppm (98 $\mu g/m^3$). These levels are similar to those frequently found in metropolitan areas. The laboratory study also demonstrated that high RH (90 percent) is a significant factor in promoting and accelerating O_3-induced fading.

Haynie et al. (1976) and Upham et al. (1976) reported on the degree of fading of three different drapery fabrics exposed in a laboratory chamber to combinations of high and low O_3 concentration (980 and 196 $\mu g/m^3$; 0.5 and 0.1 ppm, respectively), high and low RH (90 percent and 50 percent), and high and low concentrations of NO_2 and SO_2. The three fabrics selected for this study were a royal blue rayon-acetate, a red rayon-acetate, and a plum cotton duck. The samples were exposed in the chamber for periods of 250, 500, and 1000 hr; the degree of fading was measured with a color difference meter. The fading of the plum-colored material was statistically related to RH and the NO_2 concentration. For the red and blue fabrics, only RH appeared to be a significant factor. The effects of concentrations of ozone on the amount of fading of these dyes were not statistically significant, even after exposure for 1000 hr to 980 $\mu g/m^3$ (0.5 ppm), levels much higher than typical ambient exposures.

Haylock and Rush (1976, 1978) studied the fading of anthraquinone dyes on nylon fibers. In the first test, nylon carpet yarn dyed with Olive I and Olive II was exposed to varying levels of temperature, RH, and O_3. Material dyed with Olive I and exposed at 70 percent RH, 40°C (104°F), and 0.2 ppm (392 $\mu g/m^3$) of O_3 showed visible fading after 16 hr of exposure. At 90 percent RH, similar fading occurred in less than 4 hr. Under the same RH and temperature conditions, increasing the O_3 concentration from 0.2 ppm to 0.9 ppm (392 to 1760 $\mu g/m^3$) resulted in a parallel increase in fading. Samples in knitted sleeve form demonstrated much greater susceptibility to O_3 attack than samples in skein form.

Using Disperse Blue 3 and Disperse Blue 7 dyes exposed to constant conditions of 40°C (104°F), 90 percent RH, and 0.2 ppm (392 $\mu g/m^3$) of O_3, Haylock and Rush (1976) investigated the effect on fading of changing the fiber cross section, the fiber draw ratio, and the method of setting the nylon fibers with steam heat. They found that increasing the surface area of the fibers resulted in an increased fading rate. Increasing the fiber draw ratio reduced dye fading, and increasing the heat-setting temperature decreased resistance to fading in disperse dyes.

The necessity of high temperature and high humidity for induction of O_3 fading in nylon was further confirmed by the additional work of Haylock and Rush (1978). Their studies showed a good correlation between accelerated O_3 fading in the laboratory and in outdoor, in-service exposure, during which temperature and humidity extremes were common. Control samples exposed indoors, however, where temperatures and humidities were lower, did not exhibit nearly the same magnitude of fading as the laboratory samples.

Heuvel et al. (1978) investigated the importance of the physical nature of Nylon 6 yarns on the O_3 fading behavior of a disperse blue dye. Samples of Nylon 6 yarns dyed avocado green with a dye mixture including Disperse Blue 3 were exposed in a laboratory cabinet to 0.5 ppm (980 $\mu g/m^3$) of O_3 at 40°C and an RH of 85 percent. Heuvel et al. found that the microfibril diameter and specific surface area of the fiber were the fiber characteristics most closely related to O_3 fading, thus confirming suspicions expressed earlier by Salvin (1969).

Nipe (1981) summarized the results of a 3-year study to establish the relationship between in-service atmospheric contaminant fading by O_3 of carpets in a home versus O_3 fading as determined by the American Association of Textile Chemists and Colorists (AATCC) Standard Test Method 129, Colorfastness to Ozone in the Atmosphere Under High Humidities. (Measurements were also taken to compare the fading caused by oxides of nitrogen.) The test carpets were made of Nylon 6 and 66 dyed with two disperse and two acid dye formulas. Test samples from the homes of 28 participants were returned every 3 months for the 3-year period. The exposure sites selected for this long-term study represented variations in home heating and cooling, utilities, climate, and geographical locations. The carpet samples were placed in areas as close as possible to the kitchen but away from exposure to sunlight or any traffic.

Attempts were made to relate the color change for each exposure period to outside temperature and RH, but the statistical analyses of the data showed no correlation between outside weather conditions and in-home fading by either contaminant. Geographical location appeared to have a significant effect on fading. Test samples from sites in the southeast and northeast showed far more O_3 fading than those in the west and far west. Test samples in homes with air conditioning exhibited less fading during the summer than those without air conditioning. In all samples, much greater fading was caused by O_3 during July, August, and September than in January, February, and March.

Typically, O_3 levels indoors are higher during the summer, when doors and windows are more likely to be open, thus allowing a greater exchange between inside and outside air. The results of the study of in-service interior carpet exposures were compared with the results of AATCC Test 129, as shown in Table 8-8. In a sample that performs satisfactorily through 1.08 cycles of exposure in AATCC Test 129, there is a 98-percent probability against in-service fading over a 1-year period. A sample that performs satisfactorily through only 0.6 test cycles of fade has only a 90-percent probability of satisfactory performance after 1 year of in-service exposure.

Kamath et al. (1982) studied the effect of atmospheric O_3 dye fading on nylon fibers. Prior studies had postulated that O_3 does not penetrate into the fiber to destroy the dye, but instead attacks the dye at the surface of the fiber. Dye then diffuses outward from the fiber interior because of the concentration gradient set up as the surface dye is destroyed. Using microspectrophotometry to test this postulated mechanism, Kamath et al. studied the diffusion and destruction of C.I. Disperse Blue Dye 3 on Nylon 6 continuous filament yarn measuring about 45 µm in diameter. With this method, they were able to generate a dye distribution profile across the cross section of the fiber and to determine the diffusion coefficient of a dye in the fiber. The fibers were exposed in a controlled environment to O_3 concentrations of 0.2 ppm (392 $\mu g/m^3$) for 2 to 120 hr at a temperature of 40°C and RH levels of 90 percent, 85 percent, and 65 percent. The results of these laboratory studies indicated that RH has a significant positive effect on fading, that destruction of the dye begins near the surface of the fiber in the early stages of exposure, and that O_3 penetration into the fiber may be an important mechanism in O_3 fading. As shown in Figure 8-6, the dependence of fading rates on humidity was substantial. Even slight rises in humidity from 85 percent to 90 percent caused a significant increase in the extent of fading. At 65 percent RH, the fading rate drops dramatically. This effect was attributed to the breakage of hydrogen bonds in the presence of water, which leads to a more open structure with high segmented mobility; this condition is more favorable to diffusion of O_3 and disperse dyes.

Kamath et al. (1982) used a surface reaction model to attempt to explain the amount of fading (dye loss) due to O_3 exposure. They found, however, that this approach could explain only a very small portion of the loss. They concluded that the dye distribution profile across the fiber resulted from

TABLE 8-8. COLORFASTNESS OF TEST SAMPLES COMPARED WITH COLORFASTNESS OF IN-USE CARPETING

Probability of acceptable colorfastness of in-use carpeting	Number of test cycles equivalent to 1 year of in-use service	Number of test cycles equivalent to 5 years of in-use service
99	1.36	6.80
98	1.08	5.40
95	0.80	4.00
90	0.60	3.00
80	0.42	2.10
75	0.37	1.85
70	0.33	1.65
60	0.27	1.35
50	0.22	1.10

Source: Adapted from Nipe (1981).

penetration of O_3 into the fiber itself. Subsequent reaction of this O_3 with dye diffusing toward the surface of the fiber was therefore considered to be an important mechanism in O_3 fading of anthraquinone dyes in nylon.

Salvin (1969) reported that O_3 and (to a lesser extent) NO_2 caused dye fading of cotton/permanent press fabrics. As summarized by Dorset (1975), O_3 was found to be the major fading agent, with nitrogen oxides also capable of causing fading, though to a lesser extent. The fading mechanism occurs as a result of the curing operation and involves the disperse dyes on the polyester fibers rather than the vat dyes on cotton. During curing, some disperse dyes partially migrate to the permanent press finish, which is a combination of reactant resin, catalysts, softeners, and nonionic wetting agents. This migration occurs preferentially along the folds and creases, causing fading to predominate in these areas. The disperse dyes migrate to the solubilizing agents in the finish, a medium in which fading by air contaminants can easily occur. Remedial measures to avoid this problem include selecting dyes more resistant to reaction with O_3 and NO_2, avoiding the use of magnesium chloride catalyst in the permanent press process, and using different surfactants and softeners. The use of magnesium chloride as a catalyst makes O_3-sensitive dyes more sensitive to O_3 and less fast to washing (Dorset, 1975). When the catalyst is zinc nitrate, dyes are more washfast and resistant to O_3 fading. Thus, the amount of dye fading might not be a function only of O_3 concentration but also of the number of times the garment is washed. The present use

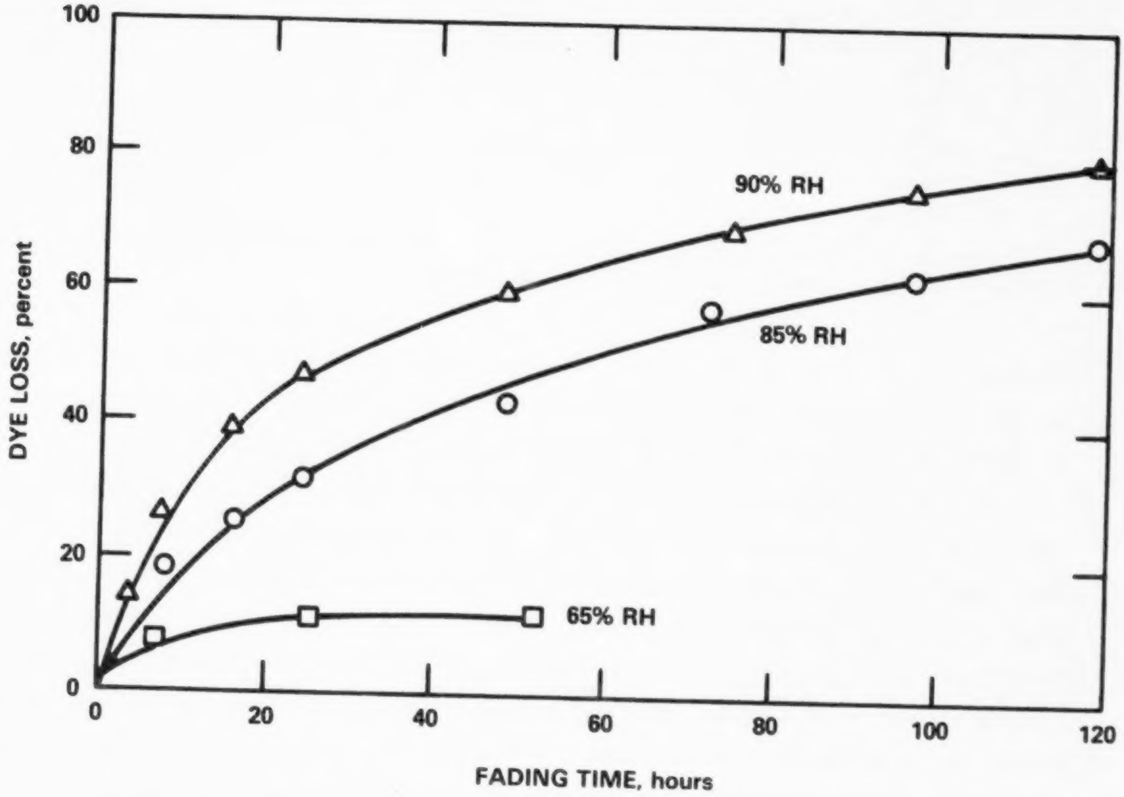

Figure 8-6. Effects of relative humidity (RH) on fading of C.I. Disperse Blue 3 (CIDB-3) in Nylon 6 after exposure to 0.2 ppm ozone.

Source: Adapted from Kamath et al. (1982).

of a zinc nitrate catalyst appears to have generally eliminated the problem of the prefading of dyes in permanent press fabrics from O_3 exposure. A summary of the dye fading studies is presented in Table 8-9.

The type of research reported on dye fading is primarily qualitative in nature. Earlier studies relied on comparisons among various geographical locations and seasonal variations with little attention given to actual concentration and exposure characterizations. For several of the initial field investigations reported here, neither ozone nor oxidant concentrations were given; rather, notations such as high versus low or urban versus rural were the only description of oxidant levels. The few laboratory studies of any technical merit employed only two concentrations of ozone at most, making it nearly impossible to derive dose-response relationships. Comparisons among studies are difficult owing to the various dye and fabric combinations tested. Also, the importance of relative humidity on ozone fading rate confounds comparisons among many of the studies that did not use the same RH percentages. Moreover, further complications arise from the absence of standardized methods to measure dye fading.

8.3.3 Fiber Damage

Sunlight, heat, alternate wetting and drying, and microorganisms are causative factors in the weathering and deterioration of fabrics exposed outdoors. The influence of O_3 at normal ambient levels is generally small by comparison.

In a review of the effects of weather and atmospheric pollutants on textiles, Warty (1977) outlined a number of damage mechanisms, the complexity of the mechanisms, and their effects on manmade and natural fibers. The damage mechanisms reviewed included those involving soiling, O_3, sunlight, microbial attack, humidity, and SO_2. Natural fibers such as jute, flax, hemp, sisal, and coconut, which have a multicellular structure and contain lignin, are much more resistant to the effects of weathering than is cotton, a natural fiber with no lignin. Even in amounts as small as 0.2 percent, however, lignin will cause yellowing or browning of the material when exposed to light. Compounds added to increase resistance to one weathering agent may actually accelerate the damage caused by others. For example, the interaction of light with phenolic compounds used as antimicrobial agents accelerates fabric degradation.

TABLE 8-9. LABORATORY STUDIES OF THE EFFECTS OF OZONE ON DYE FADING

Dye	Fabric	Concn., ppm	Exposure	Environmental Variables	Effects	Comments	Reference
Blue and red	Drapery	0.1	-	-	Both dyes were markedly bleached. No fading occurred when antioxidants were added.	Insufficient data for dose-response determinations. This study followed a field study showing that oxidants other than NO_x caused fading.	Salvin and Walker (1955)
Direct red 1	Cotton	0.05 0.5	12 2k	Temp.=130°C, 32°C RH=50%, 90%	Induced fading at both levels but at a nonlinear rate. Both temperature and humidity increased fading rate, and RH was more important. Fabrics 13, 14, 15 the most sensitive, followed by 19, 1, 17, 18, and 7. Only trace amounts of fading occurred in the remaining fabrics.	Insufficient data to show detailed dose-response relationships. Although samples were measured throughout the exposure, only the 12-wk data were presented	Beloin (1973)
Reactive red 2	"						
Sulfur green 2	"						
Azoic[a] red	"						
Direct red 1	Rayon						
Acid red 151	Wool						
Acid yellow 65	"						
Acid violet 1	"						
Basic red 14	Acrylic						
Basic yellow 11	"						
Acid orange 45	Nylon						
Disperse blue 3	"						
Disperse blue 3	Cellulose acetate						
Disperse blue 3	"						
Disperse blue 27	Polyester						
Disperse blue 27							
AATC O_3 ribbon	Acetate						
Olive I and II	Nylon fibers	0.2 0.9	1->6 hr	RH=70%-90% Temp.=40°C	Visible fading in Olive I after 16 hr at 70% RH; same effect after 4 hr at 90% RH. Linear increase in fading at 0.9 ppm O_3.	Both RH and O_3 concentration affected fading and in a nearly linear fashion. Sleeve form was more susceptible than skein form. Haylock and Rush (1976) found that: (1) increased fiber draw ratio reduced fading; (2) increased heat-setting temperature increased fading; (3) increased fiber surface area increased fading	Haylock and Rush (1976)
Disperse blue 3 and 7	Nylon fibers						
Disperse blue dye in an avocado green mixture	Nylon 6 yarn	0.5	-	RH=85% Temp.=40°C	Fading was closely correlated with fiber surface area (diameter).	Insufficient data for dose-response relationship determinations.	Heuvel et al. (1978)
Disperse blue 3	Nylon 6 yarn	0.2	2-120 hr	RH=65%, 85%, 90%, Temp.=40°C	Nearly linear increase in fading with time. RH had a major influence on fading rate.	This study focused more on mechanisms of O_3 fading rather than dose-response relationships.	Kamath et al. (1982)

[a] Coupling component 2, azoic diazo component 32.

Cellulose fibers, whether natural or manmade, are very sensitive to sunlight in the UV portion of the spectrum. Ultraviolet light causes disruption of the chemical bonds within the fiber itself. Even in protected fabrics, a secondary photochemical reaction can occur with certain dyes and pigments. Bleached fabrics, which are much more resistant to microbial attack, tend to be much more sensitive to the action of sunlight. The bleaching weakens molecular linkages, making the carbon-carbon and carbon-oxygen bonds much more easily broken when exposed to sunlight.

Synthetic fibers, though highly resistant to microbial attack, are still adversely affected by UV light. Degradation can be minimized or avoided by use of UV-absorbing additives applied as coatings or in the manufacturing process. Warty (1977) concluded that, because the weathering process is a very complex interaction of several variables, it is difficult to rely on a single test method to define performance.

Bogaty et al. (1952), as part of a program aimed at segregating some of the elements that cause weathering, carried out experiments to study the possible role of O_3 in the deterioration of cotton textiles. These investigators exposed samples of duck and print cloth to air containing 0.02 and 0.06 ppm (39 and 118 $\mu g/m^3$) of O_3. Samples were exposed both dry and wet and tested for 50 days. The wet samples were water-saturated once per week, and moisture was added regularly so that the moisture content of the cloth was never less than 50 percent. Similar fabric samples were exposed to similar O_3 concentrations with no moisture added, and another control group was similarly wetted but exposed to clean (O_3-free) air. After exposure to O_3, the wetted samples showed a loss in breaking strength of approximately 20 percent. The wet print control cloth showed a loss in breaking strength of only half this amount. The study showed that low levels of O_3 degrade cotton fabrics if they are sufficiently moist. Bogaty et al. surmised that an estimated 500 to 600 days of natural exposure might be required to reach a stage of degradation similar to that caused by a 50-day exposure to O_3 alone. Because unprotected fabrics typically reach a much more advanced state of decay after such long exposures to weathering, Bogaty et al. concluded that the effect of O_3 is slighter than that of other agents. Although not noted by Bogaty et al., the O_3 and increased moisture may have caused the formation of hydrogen peroxide (H_2O_2), which could account for the loss in breaking strength.

Morris (1966) also studied the effects of O_3 on cotton. Samples were exposed in the absence of light to 0.5 ppm (980 $\mu g/m^3$) of O_3 (more than four times the National Ambient Air Quality Stadard (NAAQS) of 235 $\mu g/m^3$ or 0.12 ppm) for 50 days in a chamber maintained at 70°F (21°C) and 72 percent RH. No appreciable effect on breaking strength was found. Apparently, the moisture content of the cotton was not high enough to produce the degradation that Bogaty et al. (1952) measured in wet cotton samples, even though the concentration of O_3 was considerably higher.

The laboratory study of Kerr et al. (1969) examined the effects of the periodic washing of dyed cotton fabrics exposed to O_3 and the amount of fading and degradation of moist, dyed fabrics exposed to O_3. They exposed samples of print cloth, dyed with CI Vat Blue 29, in a chamber to a continuous supply of purified air containing O_3 concentration levels of 1 ± 0.1 ppm (1960 ± 196 $\mu g/m^3$). The samples were exposed at room temperature (25°C) in the absence of light, and a shallow container of water was kept on the chamber floor to increase the humidity. Samples were withdrawn from the chamber after 12, 24, 36, 48, and 60 days. After an exposure period of 60 days, which included either 20 washing or 20 soaking treatments, the change in strength of control fabrics was not significant. By comparison, the fabrics exposed to O_3 changed significantly; the loss in strength of the washed fabrics was 18 percent, and that of the soaked fabrics, 9 percent. Fading was also evident in the fabrics exposed to O_3, but not in the control samples. Differences in the amount of fading between the washed and soaked samples were evident, but the reason for the differences was not. Kerr et al. concluded that washing in hot, soapy water may have affected the properties of the dye.

In laboratory studies, Zeronian et al. (1971) simultaneously exposed modacrylic (dynel), acrylic (orlon), Nylon 66, and polyester (dacron) fabrics to artificial sunlight (xenon arc) and charcoal-filtered air contaminated with 0.2 ppm (392 $\mu g/m^3$) of O_3 at 48°C (118°F) and 39 percent RH. During exposure, the fabric samples were sprayed with water for 18 min every 2 hr. Ozone damage was measured by comparing these samples with fabrics exposed to the same environmental conditions without O_3. After exposure for 7 days, Zeronian et al. found that O_3 did not affect the modacrylic and polyester fibers. The exposure did seem to affect the acrylic and nylon fibers slightly by reducing breaking strength. The degree of difference, however, in the change of fabric properties between those exposed to light and air and those exposed to light and air containing 0.2 ppm (392 $\mu g/m^3$) of O_3 was not significant.

In general, the contribution of O_3 to degradation of fabrics has not been quantified well. Bogaty et al. (1952) concluded that the effects of other factors (sunlight, heat, wetting and drying, and microorganisms) far outweighed the effects of O_3 on cotton duck and print cloth. The work by Morris (1966) and Kerr et al. (1969) does point to the synergistic effect of moisture and O_3 as an important ingredient in material degradation, possibly caused by the formation of a more potent oxidizing agent. Finally, the work of Zeronian et al. (1971) also indicates little if any effect of O_3 on synthetic fibers. Thus, it appears that O_3 has little if any effect on textiles, fibers, and synthetic cloth exposed outdoors. A similar view was proposed by the National Academy of Sciences (National Research Council, 1977) in a review of the effects of O_3 and other photochemical oxidants on nonbiological materials.

8.3.4 Paint Damage

A paint surface may suffer several types of damage that affect its usefulness, including cracking, peeling, erosion, and discoloration. Of these, erosion (i.e., wearing away of the paint surface) is the type of damage most often studied with respect to the impact of gaseous pollutants. Studies of paint cracking and peeling have focused on the effects of moisture and have not dealt with the possible influence of ambient pollutants.

Several damage functions for O_3-induced erosion of paint have been reported in the literature. Such reports are based on either accelerated chamber studies or long-term outdoor exposure studies. Unfortunately, all studies to date have significant flaws that render their results highly questionable. Damage to a paint surface is the cumulative effect of the conditions to which the surface is exposed, including various combinations of temperature, moisture, sunlight, and pollution level. No outdoor exposure study to date has been able to match all factors exactly to separate the impact of O_3 from the other factors.

In a laboratory chamber exposure study, Haynie et al. (1976) exposed oil-based house paint, latex house paint, vinyl coil coating, and acrylic coil coating to 0.5 and 0.05 ppm concentrations of SO_2, NO_2, and O_3 in various combinations. Statistically significant effects of O_3-caused damage were observed on the vinyl coil coating and the acrylic coil coating. There was a positive interaction between O_3 and RH on the vinyl coil coating and a positive direct O_3 effect on the erosion rate of the acrylic coil coating. The rate of erosion was low, however, and both vinyl and acrylic coil coatings were shown to be very durable. Coatings as thin as 20 μm should last more than 20 years before requiring replacement because of the effects of O_3. A linear regression for the acrylic coil coating data gives:

$$\text{Erosion rate} = 0.159 + 0.000714\ O_3 \qquad (8\text{-}1)$$

where erosion rate is in μm/yr and O_3 is μg/m^3.

Although the O_3 effect on this coating was found to be statistically significant, it has no practical significance because the erosion rate is so slow; at 0.12 ppm (235 μg/m^3) of O_3, the erosion rate is 0.33 μm/yr. At an average annual O_3 level of 100 μg/m^3, this regression predicts that a 20-μm-thick coating would last over 80 years.

In a comprehensive study by Campbell et al. (1974), panels painted with different exterior paints (automotive refinish, latex coating, coil coating, industrial maintenance coating, and oil-based house paint) were exposed to air pollutants in an environmental chamber under accelerated weathering conditions. The panels were exposed to low (0.1 ppm) and high (1.0 ppm) concentrations of O_3 and SO_2. After exposure, the panels were examined by measuring erosion, gloss, surface roughness, tensile strength, attenuated total reflectance (ATR), and the surface effects revealed by scanning electron microscopy and infrared examination. The panels were examined after 0, 400, 700, and 1000 hr of chamber exposure (considered as equivalent to 0, 200, 350, and 500 days, respectively, of exposure).

The relative sensitivity of a coating to pollutant damage depended on the particular test used to define the damage. For example, when comparing oil-based house paint with automotive paint, the former showed the greatest ATR change but no change in gloss, but the latter exhibited little ATR change and the largest change in gloss. In general, exposures to 1 ppm (1960 μg/m^3) of O_3 produced greater increases in erosion rates than did clean air. Concentrations of this magnitude, however, do not represent typical ambient exposure levels of O_3. At the more representative level of 0.1 ppm (196 μg/m^3), O_3 did not produce statistically significant increases in erosion rates.

In conjunction with the chamber studies, field measurements were made of the erosion of paint from test panels exposed to outdoor environments consisting of a clean, rural atmosphere (Leeds, North Dakota); a moderately polluted atmosphere (Valparaiso, Indiana); a heavily polluted (SO_2) atmosphere (Chicago, Illinois); and a high-oxidant, moderately polluted atmosphere (Los Angeles, California). The results of this study showed that paint erosion was much greater in the polluted areas than in relatively clean, rural areas. The highest erosion rates were observed for the coil coating and oil-based house paints at the Chicago and Los Angeles exposure sites. Since meteorology and air quality were not measured at the exposure sites, correlation of film damage with the environmental parameters was not possible. The study does suggest that SO_2 exerts an adverse effect on exterior paints with calcium carbonate as an extender pigment. The coil coating and oil house paints were formulated with calcium carbonate. Oxidants were probably reacting with the organic binder of the coil coating and oil house paints, although no mechanism for this reaction was developed from this exposure study.

In an outdoor exposure test of the effects of air pollutants on materials, Mansfeld (1980) exposed latex and oil-based house paints as well as galvanized steel, weathering steel, stressed aluminum, silver, marble, and nylon at nine test sites in St. Louis, Missouri. In conjunction with the material exposures, measurements of meteorological parameters, O_3, oxides of nitrogen, total hydrocarbons, total sulfur, SO_2, and hydrogen sulfide were made. The investigator used a regression model to relate the corrosion rates (i.e., rate of change of damage) to the meteorological parameters, air quality parameters, and length of exposure. There is some uncertainty in the results of the analysis because the independent variables show a degree of correlation with each other. Nevertheless, the results of several of the material-pollutant relationships are worth noting. For the latex house paint, concentrations of atmospheric O_3 were found to contribute significantly more to the accelerated erosion of the painted surface than the duration of exposure or the direction (north, south) to which the sample was exposed. The duration of exposure and the sulfate concentration were the most important factors in explaining the erosion of oil-based paint. Mansfeld suggested that these effects indicate the differing responses and behavior of the two types of paint.

Some of the color pigments used in commercial paints and dyes are also used in artists' paints. Shaver et al. (1983) studied the colorfastness of several of these pigments exposed to 0.40 ppm of O_3 for 95 days under controlled temperature and humidity conditions. Several of the 1,2-dihydroxyanthraquinone-type pigments faded considerably, but no dose-response curves could be determined. Furthermore, the effects on pigments combined with the various binders used in actual applications has not been investigated. Nevertheless, because works of art have an indefinite service life compared with, for example, the short service life for textiles, further research is needed before estimates of the type and amount of damage to paintings and prints are possible.

The effects of O_3 on paint are still being studied. The preliminary results of Mansfeld's work indicate that there may be a statistically significant relationship between the erosion of latex paint and RH and O_3. Further studies are necessary, however, before a cause-and-effect relationship can be conclusively established.

8.4 ECONOMICS

8.4.1 Introduction

Damage to nonbiological materials from ozone is usually expressed in terms one or both of the following two general classes of costs to producers and consumers: (1) ozone-accelerated replacement and repair costs, as when the service life and/or aesthetics of a material are impaired, and (2) increased avoidance costs, as when certain industries (e.g., tires, plastics, paints, dyes, and fabrics) are obligated to incur expenditures for antiozonant research and development, substitute processes and materials, additives and formulations, product packaging, advertising, etc., in order to offset sales losses that would otherwise occur.

In theory, the approach selected should depend on the observed behavior of the producers and consumers of the materials in question, and the type of damage to which they are reacting. In practice, the existing empirical estimates of ozone damage to materials are far from reliable for the following reasons:

1. In some studies, coverage is limited to one or two classes of materials, and to restricted geographical regions.
2. Other studies are entirely too aggregative, suffering deficiencies because of (1) broad and vague notions of materials exposure and ozone concentrations; (2) little or no data on the spatial and temporal distributions of the exposed materials; (3) unverified guesses regarding the incidence and level of cost increases and production adjustments incurred by ozone-affected industries; and (4) inadequate attention to economic trade-offs

among different industries and different regions, and between producers versus consumers.

3. The engineering/economic estimates are not well related to the scientific literature in this area, and tend to be far too simplistic to meet the concerns of the scientist.

4. Most of the cost assessments were conducted in the early 1970s. Few recent studies exist. Moreover, these earlier studies cite extensively from each other and there are few independent analyses that do not merely rework old data.

5. As a consequence of the fourth item above, many of the ozone-related costs reported in the early 1970s for research and development, product substitution, etc., are no longer appropriate. Some of these were presumably once-only costs that are no longer charged against current production. Because the literature is dated, there may also be some current research and development, substitution attempts, and so on, not at all reflected in the studies cited in this section. In sum, the cost estimates largely reflect technologies and ozone concentrations prevailing some 10 to 20 years ago.

6. Most of the so-called economic studies of ozone damage to materials have been conducted using an engineering approach. That approach focuses on the classification and quantification of the various kinds of costs incurred by the producers and users of the ozone-sensitive materials. Economic theory would argue, however, that this is merely the first step in the assessment process, and that supply-demand relationships are then needed in order to proceed with the calculation of social net benefits (i.e., changes in producer and consumer surpluses). In practice, however, it appears that almost all of the damage assessments conducted to date stop short of obtaining an econometric measure of economic surplus. As such, the studies reported in this section must be interpreted accordingly.

8.4.2 Methods of Cost Classification and Estimation

Computation of accelerated replacement is probably the most widely applied method of estimating the costs of materials damage to air pollutants. In this approach a materials damage function is developed to show the increase in physical damage for an increase in the dose of the pollutant. Then a cost schedule is constructed to show how maintenance or replacement schedules are influenced by the pollutant level. Hershaft et al. (1978) note, however, that this method usually assumes existing inventories, and does not take into account substitutions of materials with more (or less) resistance to pollution. As a result, this method tends to overestimate the cost of damage from pollutant increases and to underestimate the net savings realized from pollutant reductions.

A second approach considers avoidance costs. This refers to practices such as adopting alternative production processes and materials. Some industries add antiozonants to their products, or change the chemical formulation of their output. All of these measures mitigate the impact of ozone on the service life or aesthetics of the products in question. Moreover, these measures also require research, development, and implementation expenditures. As such, estimation of these costs is conceptually and empirically difficult, since the opportunity to use different materials changes in response to the level of ozone concentration.

A number of factors complicate the use of both the replacement and the avoidance methodologies. Data on key variables are generally missing or merely assumed. Lessening the reliability of the final cost estimates are deficiencies in knowledge of (1) the physical damage functions; (2) the quantities and types of materials exposed to ozone indoors, outdoors, and in respective regions of the country; (3) the actual expenditures incurred for increased replacement, maintenance, and avoidance that can be directly attributed to ozone; (4) the threshold ozone damage levels that prompt mitigating action; and (5) the range of substitution strategies that can be used to ameliorate degradation. On this latter point, few attempts have been made to identify current technology practices and possibilities. The variety of rubber compounds, paint mixtures, and fabric dyes reflects the number of proprietary formulations, and each formulation presumably has a different response to ozone exposure.

An additional complication is that repair, replacement, and substitution are frequently dominated by factors unrelated to ozone concentrations. This can lead to spurious correlations if studies are accepted uncritically. For example, tire replacement may be high in a given region of the country because of high ozone levels associated with automotive exhaust. Alternatively, it may be high simply because the total miles of automotive use per year are higher in that region than in the nation as a whole.

Another illustration is the substitution of dyes. New dyes that replace ozone-sensitive dyes may also be more colorfast and able to survive more washings than the dyes they replace. In this case, apportionment of the costs of the new dyes between ozone resistance and the other improved characteristics embodied in the new formulations is an extremely arbitrary and perhaps meaningless exercise.

8.4.3 Aggregate Cost Estimates

The important caveats identified in the preceding discussion qualify the empirical data presented in this and following sections. Table 8-10 summarizes reports of highly aggregated estimates of oxidant damage to all materials. Unfortunately, there are no known recognized studies that are more recent than those reported in the table. For purposes of gross comparison only, the figures are expressed in 1984 currency equivalents alongside 1970 currency equivalents, the base data for the reference studies. They do not, however, represent 1984 supply-demand relationships, production technologies, or ozone concentrations. It must be emphasized that the costs cited in 1984 currency equivalents therefore cannot be considered true 1984 costs.

TABLE 8-10. SUMMARY OF DAMAGE COSTS TO MATERIALS BY OXIDANTS
(in millions of 1970 and 1984 dollars)

Study	Materials costs		
	Elastomers/plastics	Fabric/dye	All
Barrett and Waddell (1973)	ND[a]	(260)	(3878)
Mueller and Stickney (1970)	500.0 (1500)[b]	ND	ND
Salmon (1970)	295.2 (915)	358.4 (1111)	653.6 (2026)
Salvin (1970)	ND	83.5 (259)	ND
Waddell (1974)	ND	ND	900.0 (2790)
Yocum and Grappone (1976)	ND	ND	572.0 (1773)
Freeman (1979)	ND	ND	505.0 (1566)

[a] ND=No data. Investigator(s) did not develop estimates in this category.

[b] 1984 dollars are listed parenthetically below 1970 dollars and reflect inflation (consumer price index) rather than real increases in costs.

Salmon (1970) was among the first to attempt to estimate the annual cost of air pollution damage to materials. His computation included the dollar value of annual materials production, a weighted average economic life of each material included in his study, a weighted average factor for the percentage of the material exposed to air pollution, and a factor for increased labor to treat damaged materials. Cost was defined as the value of the material multiplied by the difference between the rate of material deterioration in a polluted urban versus an unpolluted rural environment. All data, except for annual production levels of materials, were assumed.

If it is assumed that ozone affected all of the fibers, plastics, and rubber in the study by Salmon, then annual damage costs attributed to ozone would have been $2,026 million (1984$). Salmon did not consider ozone-related damage to paint, since the dominant paint-damaging mechanisms are soiling and gaseous sulfur dioxide. His costs refer to maintenance and replacement only, and do not allow for materials protection, substitution, etc.

In discussing other limitations of his study, Salmon cautioned that his estimates were of potential loss, not of actual observed loss. Despite this and other qualifications that lessen the usefulness of the figures derived, the Salmon study has been cited extensively and used quantitatively in a number of the subsequent studies cited here.

For example, the materials estimate by Barrett and Waddell (1973) is based primarily on the work of Salmon (1970). Barrett and Waddell supplemented this by drawing on Mueller and Stickney (1970) for damage costs on elastomers, and on Salvin (1970) for damage costs related to dye fading. Combining some of these numbers, Barrett and Waddell stated that materials damage costs attributable to oxidants alone were $3,878 million (1984$).

Freeman (1979) reviewed earlier studies that categorized the cost of damage to materials. Using the work of Waddell (1974) and Salvin (1970), Freeman calculated that the materials damage costs attributable to oxidants and oxides of nitrogen were $2,031 million (1984$). Of this total, roughly 46 percent was damage to textiles and dyes (from Salvin 1970), while the remaining 54 percent was damage to elastomers (from Mueller and Stickney, 1970). Freeman then assumed a 20 percent reduction in oxidant levels since 1970, and went on to conclude that the monetary benefits of controlling oxidants, oxidant precursors, and oxides of nitrogen were between $170 and $510 million (1984$). Freeman computed the savings attributable to oxidant controls alone as $128 to $383 million (1984$).

Waddell (1974) likewise depended primarily on existing studies to calculate the national cost of air pollution in 1970. Waddell used Salmon (1970), Salvin (1970), Mueller and Stickney (1970), and Spence and Haynie (1972) to derive an estimate of $6,820 million (1984$) as the total gross annual damage for materials losses in 1970 resulting from air pollution. The component attributable to ozone and oxidants alone was $2,790 million (1984$), within a wide range of $1,550 to $4,030 million (1984$).

Yocom and Grappone (1976), in work for the Electric Power Research Institute, estimated that the cost of air pollution damage to materials was about $6,820 million (1984$) in 1970. Of this total, ozone was estimated to be responsible for $1,773 million (1984$), or some 26 percent of the total.

Because of the reliance of the later studies on the questionable data and unverified assumptions contained in the earlier ones, the results compared here are of extremely limited usefulness for cost-benefit purposes. The empirical estimates of materials damage at the aggregate level are typified by a paucity of original research, primary data, and fresh insights. Rather, successive layers of estimates have been generated upon essentially the same weak foundations. No recent research (e.g., post-1979) is available to improve upon this circumstance.

8.4.4 Damage to Elastomers

The damage to rubber and other elastomers by ozone can be significant in terms of the kinds and quantities of materials that are susceptible. For example, damage to rubber seals, hoses, belts, cables, pharmaceutical goods, and vehicle tires has been mentioned as economically important (Mueller and Stickney, 1970).

If damage induced by pollutants is to be considered economically important, however, the effective useful life of the product must be significantly affected by pollutant exposure. The life of many rubber products is determined more by their end use and the wear and tear of normal use than by pollutant damage. For example, the rubber in surgical gloves can be shown to be sensitive to ozone exposure. Because these gloves are used indoors, however, and because they also are usually discarded after one use, the outdoor ozone concentration has no influence on their useful lifetime.

Vehicle tires represent the major use of rubber that is subject to significant economic costs from the effects of ozone (McCarthy et al., 1983). The amount of antiozonants added to a tire formulation depends on two factors: ozone concentrations and expected tire life. Previously, tire manufacturers varied the amount of antiozonants regionally, depending on ozone concentrations. Now, however, most companies produce for a national market from each plant, and consequently formulate their compounds for worst-case conditions with an appropriate margin for safety.

The second factor that determines the amount of antiozonants in tire formulations is expected tire life. Antiozonants are added in sufficient quantities to resist ozone damage for 5 or 6 years in radial tires, and 3 or 4 years in bias-ply and bias-belted tires.

The cost of antiozonants is about $0.80 (1984$) per passenger car tire and about $1.66 (1984$) per truck tire. Given a yearly national production of 100 million passenger tires and 50 million truck tires, the total annual cost of antiozonants is $163 million (1984$). If ozone should be reduced, it is uncertain to what extent tire manufacturers would find it possible and profitable to reduce the level of antiozonants.

Mueller and Stickney (1970) contend that if ozone concentrations were reduced, but the amount of antiozonant per tire was not reduced, more retreadable tire casings would be available for passenger cars. (Truck tires have a comparatively shorter useful economic life and ozone damage is not a significant factor in truck tire retreading). In 1980, nearly 17 million tires were rejected for retreading because of weatherchecking, at least some of which was attributable to ozone. Hence, a reduction in ozone levels could conceivably make available a greater supply of retreadable tire casings, lowering costs in the retread industry. As qualified previously, however, this depends on the extent to which tire manufacturers find it economical to adjust their levels of antiozonant.

Mueller and Stickney (1970) estimated that the damage costs to elastomeric compounds caused by air pollutants, mainly ozone, totaled $1550 million (1984$). Their estimates are presented in Table 8-11. Protection against the effects of ozone (i.e., avoidance costs) represents the added cost of antiozonants, antioxidants, and special rubber blends formulated for their oxidant-resistant and ozone-resistant properties. The second cost element is early replacement because of shortened service life, a cost borne directly by consumers. The heading "indeterminate" refers to the costs of protective wrappings and coatings and research to formulate resistant compounds, and "other" includes labor

TABLE 8-11. SUMMARY OF DAMAGE COSTS TO RUBBER BY OZONE
(in millions of 1970 and 1984 dollars)[a]

	Protection[b,c]		Early replacement[d]		Indeterminate	Other	All Factors
Total cost	170(527)		225.7(700)		78(242)	~25(78)	~500(1550)
Cost breakdown	Special polymer	20.6 (64)	Tires	37.0(115)			
	Antiozonant	34.1(106)	Mechanical	29.7(90)			
	Wax	5.0(16)	Medical	100.5(312)			
			Belting	22.5(70)			
			Hose	36.0(112)			

[a] 1984 dollars are given parenthetically next to 1970 dollars.

[b] Retail value approximately three times the manufacturing cost.

[c] Smaller costs for protective finishes, wrapping, and compound development could not be estimated.

[d] Labor costs associated with replacement can be greater than the cost of the part, but realistic estimates could not be made.

Source: Mueller and Stickney (1970).

costs for repair and replacement. Although estimates are given, the authors note that these two columns really cannot be estimated. All of the costs presented in the table refer to the year 1969, are expressed in 1970 dollars, and have uncertain reliability and relevance in the context of 1984.

8.4.5 Damage to Fibers and Dyes

Ozone has a significant impact on certain sensitive dyes. Barrett and Waddell (1973) reported that the national cost of dye fading caused by ozone was $260 million (1984$) per year. Of this amount, 30 percent was dye fading in acetate and triacetate, 50 percent was dye fading in nylon carpets, and 20 percent was dye fading of permanent press garments. Barrett and Waddell assumed that avoidance costs included preventive measures to minimize damage, such as use of more expensive dyes as well as additional research and testing. Replacement costs took account of the assumed reduced life of the dyed materials.

No research has been conducted since 1973 to verify or update these estimates. A problem with them is that a proportion of fading and physical wear was arbitrarily assigned to ozone rather than to other factors. As noted previously, the use of magnesium chloride as a catalyst in the permanent-press process led to dyes that were more sensitive to ozone and also less washfast. Thus, the rate of fading is caused not only by the interaction between the dye and ozone, but also by the frequency of washing.

Salvin (1970) conducted a study on how ozone and the oxides of nitrogen increase the costs of fading of dyed fabrics. Costs in the work of Salvin included those for more resistant dyes, inhibitors, research and development, and reduced service life. Of the total cost of dye fading, that part attritubed to ozone was $259 million (1984$) per year. Salvin contacted manufacturers to obtain costs of dyes, processes, and preventive measures. The costs of reduced service life were based, however, on estimates rather than observations. Salvin's study does not seem to take into account the differences between indoor and outdoor ozone concentrations and the significance of this for textile exposure; thus, the result must be viewed cautiously for that reason.

8.4.6 Damage to Paint

Ozone levels typically occurring in the ambient air (Chapter 5) have not been shown to cause damage to paint. Campbell et al. (1974) were unable to demonstrate a relationship between ozone and paint damage either in a carefully controlled chamber study or in outside exposure tests. Haynie and Upham

(1971) showed that the only statistically significant effects of ozone on paint were damage to vinyl and acrylic coil coatings; however, the effects of ozone were insignificant in shortening coating lifetimes. McCarthy et al. (1981) found that the costs associated with premature replacement of acrylic and vinyl coil coatings were minimal and could not be attributed to pollutants alone.

Aesthetics tend to be a decisive factor in the use of acrylic and vinyl coatings. Although the coating retains its primary function of providing a protective surface, changes in gloss and sheen, as well as degradation of color, can be problems. The causative agents for these aesthetic effects are environmental factors (primarily sunlight), as well as the qualities of the pigment, formulation and mixing, and application. No data are available to suggest the role of ozone (alone or in conjunction with other pollutants) in this fading. Hence, the costs of diminished aesthetics attributable to ozone are largely undetermined.

8.5 SUMMARY AND CONCLUSIONS

Over two decades of research show that ozone damages certain nonbiological materials; the amount of damage to actual in-use materials, however, is poorly characterized. Knowledge of indoor/outdoor ozone gradients, for example, has expanded considerably in recent years, and this type of exposure information has not been incorporated in materials damage studies. Moreover, virtually all materials research on photochemical oxidants has focused on ozone. Theoretically, a number of the less abundant oxidants may equal or surpass ozone in reactivity with certain materials, but this possibility has not been tested empirically. In the absence of photochemical pollution, oxidative damage to certain materials still occurs from atmospheric oxygen, but at a much reduced rate and through different chemical mechanisms. Generally, ozone damages elastomers by cracking along the line of physical stress, whereas oxygen causes internal damage to the material.

The materials most studied in ozone research are elastomers and textile fibers and dyes. Natural rubber and synthetic polymers of butadiene, isoprene, and styrene, used in products like automobile tires and protective outdoor electrical coverings, account for most of the elastomer production in the United States. The action of ozone on these compounds is well known, and dose-response relationships have been established and corroborated by several studies. These relationships, however, must be correlated with adequate exposure information based on product use. For these and other economically important materials, protective measures have been formulated to reduce the rate of oxidative damage. When antioxidants and other protective measures are incorporated in elastomer production, the dose-cracking rate is reduced considerably, although the extent of reduction differs widely according to the material and the type and amount of protective measures used.

The formation of cracks and the depth of cracking in elastomers are related to ozone dose and are influenced greatly by humidity and mechanical stress. Dose is defined as the product of concentration and time of exposure. The importance of ozone dose was demonstrated by Bradley and Haagen-Smit (1951), who used a specially formulated ozone-sensitive natural rubber. Samples exposed to ozone at a concentration of 20,000 ppm cracked almost instantaneously, and those exposed to lower concentrations took a proportionately longer time to crack. At concentrations of 0.02 to 0.46 ppm, and under 100-percent strain, the cracking rate was directly proportional to the time of exposure, from 3 to 65 min.

Similar findings were reported by Edwards and Storey (1959), who exposed two SBR elastomers to ozone at a concentration of 0.25 ppm for 19 to 51 hr under 100-percent strain. With ozone doses of 4.75 ppm-hr to 12.75 ppm-hr, a proportional rate in cracking depth was observed, averaging 2.34 μm/hr for cold SBR and 4.01 μm/hr for hot SBR. When antiozonants were added to the compounds, the reduction in cracking depth rate was proportional to the amount added. Haynie et al. (1976) exposed samples of a tire sidewall to ozone at concentrations of 0.08 and 0.5 ppm for 250 to 1000 hr under 10 and 20 percent-strain. Under 20-percent strain, the mean cracking rate for 0.08 ppm was 1.94 μm/hr. From these and other data, they estimated that at the ozone standard of the time (0.08 ppm, 1-hr average), and at the annual NO_x standard of 0.05 ppm, it would take 2.5 years for a crack to penetrate cord depth.

In addition to stress, factors affecting the cracking rate include atmospheric pressure, humidity, sunlight, and other atmospheric pollutants. Veith and Evans (1980) found a 16-percent difference in cracking rates reported from laboratories located at various geographic elevations.

Ozone has been found to affect the adhesion of plies (rubber-layered strips) in tire manufacturing. Exposure to ozone concentrations of 0.05 to 0.15 ppm for a few hours significantly decreased adhesion in an NR/SBR blend, causing a 30-percent decrease at the highest ozone level. This adhesion problem worsened at higher relative humidities. When fast-blooming waxes and antiozonants or other antioxidants were added, only the combination of protective measures allowed good adhesion and afforded protection from ozone and sunlight attack. Wenghoefer (1974) showed that ozone (up to 0.15 ppm), especially in combination with high relative humidity (up to 90 percent), caused greater adhesion losses than did heat and NO_2 with or without high relative humidity.

The effects of ozone on dyes have been known for nearly three decades. In 1955, Salvin and Walker exposed certain red and blue anthraquinone dyes to a 0.1 ppm concentration of ozone and noted fading, which until that time was thought to be caused by NO_2. Subsequent work by Schmitt (1960, 1962) confirmed the fading action of ozone and the importance of relative humidity in the absorption and reaction of ozone in vulnerable dyes. The acceleration in fading of certain dyes by high relative humidity was noted later by Beloin (1972, 1973) at an ozone concentration of 0.05 ppm and relative humidity of 90 percent. Kamath et al. (1982) also found that a slight rise in relative humidity (85 to 90 percent) caused a 20-percent dye loss in nylon fibers.

Both the type of dye and the material in which it is incorporated are important factors in a fabric's resistance to ozone. Haynie et al. (1976) and Upham et al. (1976) found no effects from ozone concentrations of 0.1 to 0.5 ppm for 250 to 1000 hr under high and low relative humidity (90 vs. 50 percent) on royal blue rayon-acetate, red rayon-acetate, or plum cotton. On the other hand, Haylock and Rush (1976, 1978) showed that anthraquinone dyes on nylon fibers were sensitive to fading from ozone at a concentration of 0.2 ppm at 70 percent relative humidity and 40°C for 16 hr. Moreover, the same degree of fading occurred in only 4 hr at 90 percent relative humidity. At higher concentrations, there was a parallel increase in fading. Along with Heuvel et al. (1978) and Salvin (1969), Haylock and Rush (1976, 1978) noted the importance of surface area in relation to the degree of fading. In explaining this relationship, Kamath et al. (1982) found that ozone penetrated into the fiber itself and caused most of the fading through subsequent diffusion to the surface.

Field studies by Nipe (1981) and laboratory work by Kamath et al. (1982) showed a positive association between ozone levels and dye fading of nylon materials at an ozone concentration of 0.2 ppm and various relative humidities. In summary, dye fading is a complex function of ozone concentration, relative humidity, and the presence of other gaseous pollutants. At present, the available research is insufficient to quantify the amount of damaged material attributable to ozone alone. Anthraquinone dyes incorporated into cotton and nylon fibers appear to be the most sensitive to ozone damage.

The degradation of fibers from exposure to ozone is poorly characterized. In general, most synthetic fibers like modacrylic and polyester are relatively resistant, whereas cotton, nylon, and acrylic fibers have greater but varying sensitivities to the gas. Ozone reduces the breaking strength of these fibers, and the degree of reduction depends on the amount of moisture present. Under laboratory conditions, Bogaty et al. (1952) found a 20 percent loss in breaking strength in cotton textiles under high-moisture conditions after exposure to a 0.06 ppm concentration of ozone for 50 days; they equated these conditions to a 500- to 600-day exposure under natural conditions. Kerr et al. (1969) found a net loss of 9 percent in breaking strength of moist cotton fibers exposed to ozone at a concentration of 1.0 ppm for 60 days. The limited research in this area indicates that ozone in ambient air may have a minimal effect on textile fibers, but additional research is needed to verify this conclusion.

The effects of ozone on paint are small in comparison with those of other factors. Past studies have shown that, of various paints, only vinyl and acrylic coil coatings are affected, and that this impact has a negligible effect on the useful life of the material coated. Preliminary results of current studies have indicated a statistically significant effect of ozone and relative humidity on latex house paint, but the final results of those studies are needed before conclusions can be drawn.

For a number of important reasons, the estimates of economic damage to materials are far from reliable. Most of the available studies are now outdated in terms of the ozone concentrations, technologies, and supply-demand relationships that prevailed when the studies were conducted. Additionally, little was (and is) known about the physical damage functions, and cost estimates were simplified to the point of not properly recognizing many of the scientific complexities of the impact of ozone. Assumptions about exposure to ozone generally ignored the difference between outdoor and indoor concentrations. Also, analysts have had difficulty separating ozone damage from other factors affecting materials maintenance and replacement schedules. For the most part, the studies of economic cost have not marshalled factual observations on how materials manufacturers have altered their technologies, materials, and methods in response to ozone. Rather, the analysts have merely made bold assumptions in this regard, most of which remain unverified through the present time.

Even more seriously, the studies followed engineering approaches that do not conform with acceptable methodologies for measuring economic welfare. Almost without exception, the studies reported one or more types of estimated or assumed cost increases borne by materials producers, consumers, or both. The recognition of cost increase is only a preliminary step, however, towards evaluating economic gains and losses. The analysis should then use these cost data to proceed with supply and demand estimation that will show how materials prices and production levels are shifted. Because the available studies fail to do this, there is a serious question as to what they indeed measure.

Increased ozone levels increase sales for some industries even as they decrease welfare for others. For example, manufacturers of antiozonants for automobile tires conceivably stand to increase sales as ozone increases, while purchasers of tires stand to pay higher prices. This is only one illustration of a fundamental analytical deficiency in the various studies of materials damage: the absence of a framework for identifying gainers and losers, and the respective amounts they gain and lose.

Among the various materials studies, research has narrowed the type of materials most likely to affect the economy from increased ozone exposure. These include elastomers and textile fibers and dyes. Among these, natural rubber used for tires is probably the most important economically for the following reasons: (1) significant ambient air exposure and long use life; (2) significant unit cost; and (3) large quantities and widespread distribution.

The study by McCarthy et al. (1983) calculated the cost of antiozonants in tires for protection against ozone along with the economic loss to the retread industry. While limitations in this study preclude the reliable estimation of damage costs, the figures indicate the magnitude of potential damage from exposure to ozone in ambient air.

Research has shown that certain textile fibers and dyes and house paint are also damaged by ozone, but the absence of reliable damage functions make accurate economic assessments impossible. Thus, while damage to these materials is undoubtedly occurring, the actual damage costs cannot be estimated confidently.

It is apparent from the review presented in this chapter that a great deal of work remains to be done in developing quantitative estimates of materials damage from photochemical oxidant exposures. This is not meant to deprecate the years of research reported in this document, for much has been gained in refining the initial methodologies used for assessing damage. Yocom et al. (1985) have summarized the current state of knowledge:

> We have learned that some costs may be difficult to quantify either because they are minimal or because they are overshadowed by other factors, such as wear or obsolescence. We have learned that damage functions are complex and are influenced by the presence of other pollutants and by weather. We have learned that more accurate estimates of materials in place may be obtained using selective sampling and extrapolation. And we have learned that a mere cost-accounting of damage does not present a true estimate of economic cost if it does not account for the welfare effects induced by shifts in the supply-demand relationship.

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APPENDIX 8A.

CHEMICAL ABBREVIATIONS USED IN THE TEXT

CBS	N-Cyclohexyl-2-benzothiazole sulphenamide
6PPD	N-phenyl-N'(1,3 dimethylbutyl)-p-phenylenediamine
IPPD	N-Isopropyl-N'-phenyl-p-phenylenediamine
77PD	N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine
DTPD	Di-tolyl-p-phenylenediamine
TMQ	1,2-Dihydro-2,2,4-trimethylquinoline, polymerized
ETMQ	6-Ethoxy-2,2,4-trimethylquinoline
ADPA	Acetone diphenylamine condensate
MBI	2-Mercaptobenzimidazole
TBMP	4,4'-Thiobis (2-tertbutyl-5-methylphenol)

COMPOUND DETAILS

NR	NR, 100; HAF, 65; Oil, 3; Stearic Acid, 1; Zinc Oxide, 5; Sulphur, 2.5; CBS, 0.6
NR/SBR	NR, 50; SBR, 50; HAF, 50; Oil, 8; Stearic Acid, 2; Zinc Oxide, 4; Sulphur, 2.5; CBS, 1
SBR	SBR, 100; HAF, 50; Oil, 8; Stearic Acid, 2; Zinc Oxide, 4; Sulphur, 2.5; CBS, 1.2
IR	IR, 100; HAF, 65; Oil, 3; Stearic Acid, 1; Zinc Oxide, 5; Sulphur, 2.5; CBS, 0.6

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